

Unit 4: THERMOCHEMISTRY AND NUCLEAR CHEMISTRY

Chapter 6: Thermochemistry

6.1: The Nature of Energy

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

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** ($\Sigma E_{\text{initial}} = \Sigma E_{\text{final}}$).

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**.

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.

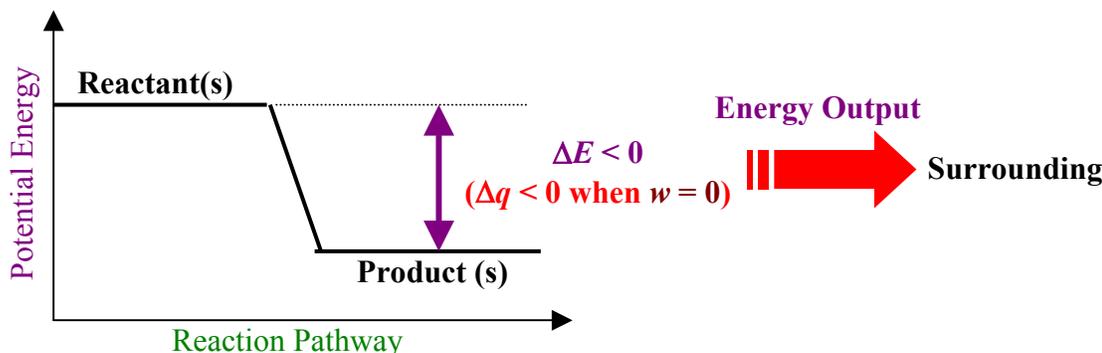
State Function: - also refer to as **State Property** of a system at its present conditions.
- energy is a state function because of its independence of pathway, whereas work and heat are not state properties.

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

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

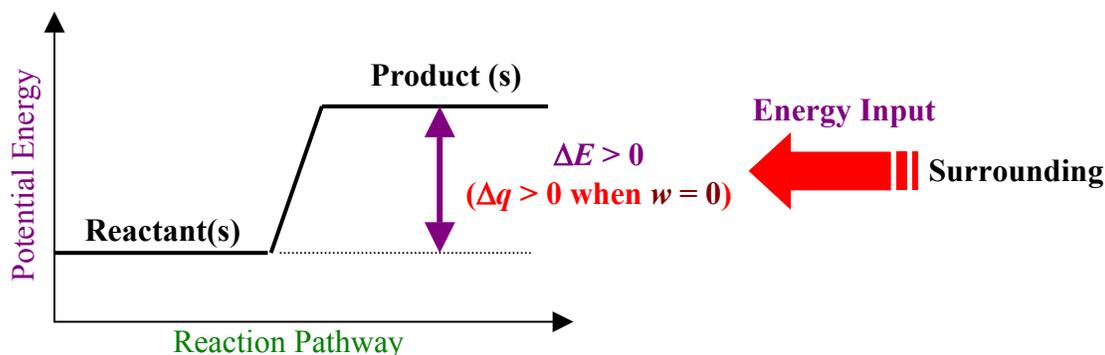
Exothermic ($\Delta E < 0$): - when **energy flows “out” of the system** into the surrounding.
(Surrounding gets Warmer.)

Potential Energy Diagram for Exothermic Process



Endothermic ($\Delta E > 0$): - when energy flows into the system from the surrounding.
(Surrounding gets Colder.)

Potential Energy Diagram for Endothermic Process



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)

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

$$q = -45 \text{ kJ (exothermic)}$$

$$w = +12 \text{ kJ (work done on the system)}$$

$$\Delta E = ?$$

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

$$\Delta E = -33 \text{ kJ}$$

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

$$q = +850 \text{ kJ (endothermic)}$$

$$\Delta V = 0.0700 \text{ L} - 12.5 \text{ L} = -12.43 \text{ L}$$

$$P = 1.25 \text{ atm}$$

$$\Delta E = ?$$

$$\Delta E = q + w = q + (-P \Delta V)$$

$$\Delta E = (+850 \text{ kJ}) + (-1.25 \text{ atm} \times -12.43 \text{ L} \times 0.1013 \text{ kJ} / (\text{L} \cdot \text{atm}))$$

$$\Delta E = +852 \text{ kJ}$$

6.2: Enthalpy and Calorimetry

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

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

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

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

Change in Enthalpy in a Chemical Reaction

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

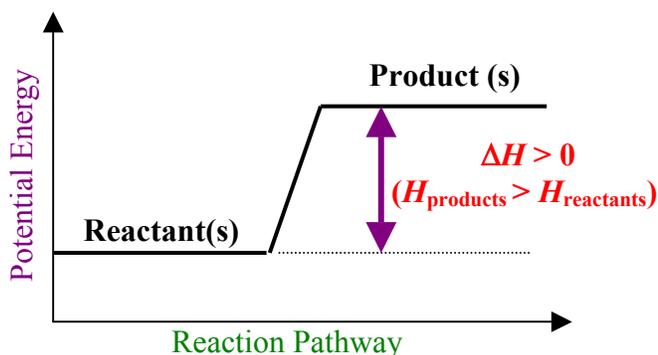
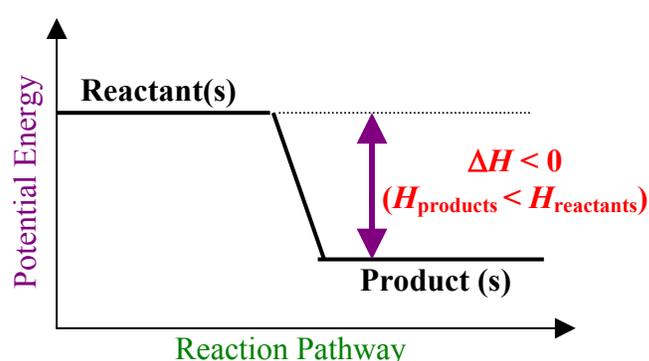
$$\Delta H > 0 \text{ Endothermic Reaction}$$

$$\Delta H < 0 \text{ Exothermic Reaction}$$

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

$$\Delta H = \text{Change in Enthalpy} \quad n = \text{moles}$$

$$\Delta H_{\text{rxn}} = \text{Molar Enthalpy of Reaction (kJ/mol)}$$

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 127.5 kJ to form 84.0 L of $\text{NO}_2(\text{g})$ from its elements at STP. Determine the molar heat of enthalpy for the formation of $\text{NO}_2(\text{g})$. Express the answer in proper ΔH notation.

$$\begin{aligned} \Delta H &= 127.5 \text{ kJ} \\ V &= 84.0 \text{ L} \\ \text{STP} &= 22.4 \text{ L/mol} \\ n &= ? \quad \Delta H_{\text{rxn}} = ? \end{aligned} \quad n = \frac{84.0 \text{ L}}{22.4 \text{ L/mol}} = 3.75 \text{ mol}$$

$$\Delta H = n\Delta H_{\text{rxn}} \quad \Delta H_{\text{rxn}} = \frac{\Delta H}{n} = \frac{127.5 \text{ kJ}}{3.75 \text{ mol}} \quad \Delta H_{\text{rxn}} = 34.0 \text{ kJ/mol}$$

$$\text{or} \quad \begin{aligned} \text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) &\rightarrow 2 \text{NO}_2(\text{g}) \quad \Delta H = 68.0 \text{ kJ} \quad (2 \text{ mol of NO}_2 \text{ in Eq}) \\ \frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) &\rightarrow \text{NO}_2(\text{g}) \quad \Delta H = 34.0 \text{ kJ} \end{aligned}$$

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

$$\Delta H_{\text{rxn}} = \frac{5317 \text{ kJ}}{2 \text{ mol}} = 2658.5 \text{ kJ/mol} \quad (\text{There are 2 moles of C}_4\text{H}_{10} \text{ in the chemical equation for 5317 kJ.})$$

$$n = \frac{28.2 \text{ g}}{58.123 \text{ g/mol}} \quad \Delta H = n\Delta H_{\text{rxn}} = (0.4851779846 \text{ mol}) (2658.5 \text{ kJ/mol})$$

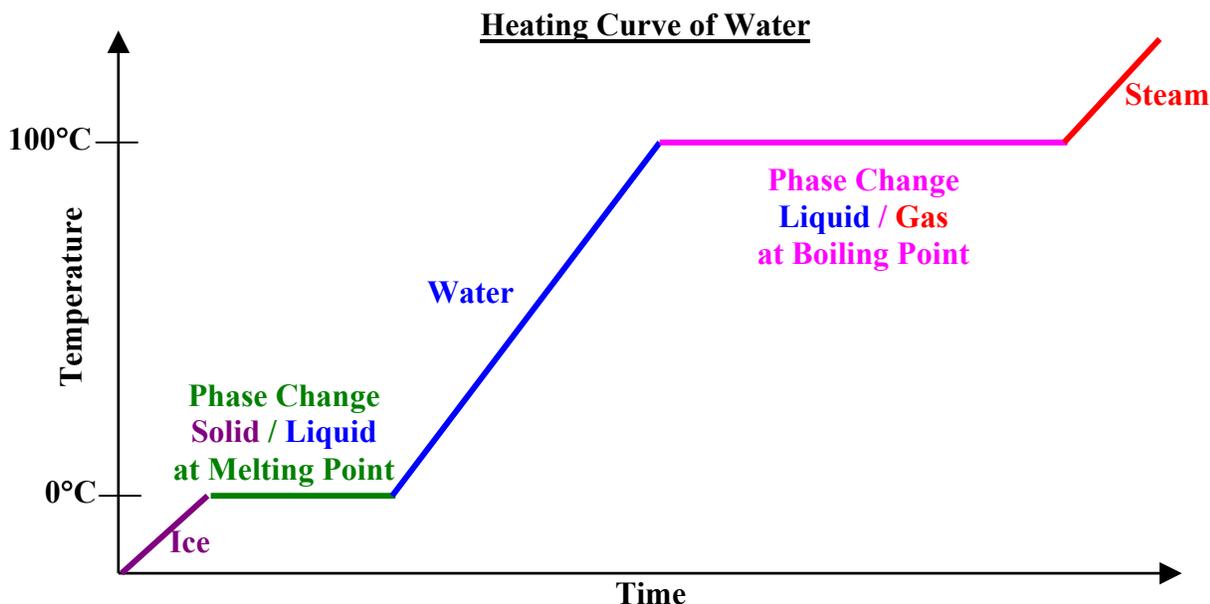
$$n = 0.4851779846 \text{ mol C}_4\text{H}_{10} \quad \Delta H = 1.29 \times 10^3 \text{ kJ} = 1.29 \text{ MJ}$$

$$\Delta H = ? \quad (1 \text{ MJ} = 1000 \text{ kJ})$$

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)

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

<u>Physical Potential Change</u>	
$\Delta H = n\Delta H_{\text{fus}}$	$\Delta H = n\Delta H_{\text{vap}}$
$\Delta H = \text{Change in Enthalpy}$	$n = \text{moles}$
$\Delta H_{\text{fus}} = \text{Molar Enthalpy of Fusion (kJ/mol)}$	
$\Delta H_{\text{vap}} = \text{Molar Enthalpy of Vaporization (kJ/mol)}$	
<u>Physical Kinetic Change</u>	
$\Delta H = mC\Delta T$	
$\Delta H = \text{Change in Enthalpy (J or kJ)}$	$m = \text{mass (g or kg)}$
$C = \text{Specific Heat Capacity}$	
$[\text{J}/(\text{g} \cdot ^\circ\text{C}) \text{ or } \text{kJ}/(\text{kg} \cdot ^\circ\text{C}) \text{ or } \text{J}/(\text{g} \cdot \text{K}) \text{ or } \text{kJ}/(\text{kg} \cdot \text{K})]$	
$\Delta T = \text{Change in Temperature (in } ^\circ\text{C or K)}$	

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

Substance	Melting Point (°C)	Boiling Point (°C)	Specific Heat Capacity [kJ/(kg • °C)]	ΔH_{fus} (kJ/mol)	ΔH_{vap} (kJ/mol)
Ice H ₂ O _(s)	0	----	2.03	6.01	----
Water H ₂ O _(l)	----	100	4.18	----	40.65
Steam H ₂ O _(g)	----	----	2.02	----	----
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	2.44	4.93	38.56
Aluminum Al _(s)	660	2519	0.897	10.79	294
Carbon (graphite) C _(s)	3338	4489	0.709	117	----
Copper Cu _(s)	1085	2562	0.385	12.93	300.4
Iron Fe _(s)	1538	2861	0.449	13.81	340
Mercury Hg _(l)	-39	357	0.140	2.29	59.1

Example 3: 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 $\Delta H = n\Delta H_{\text{vap}}$.

$$\Delta H_{\text{vap}} = 40.65 \text{ kJ/mol}$$

$$n = \frac{36.04 \text{ g}}{18.0158 \text{ g/mol}} = 2.000466257 \text{ mol H}_2\text{O}$$

$$\Delta H = ?$$

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

$$\Delta H = (2.000466257 \text{ mol})(40.65 \text{ kJ/mol})$$

$$\Delta H = 81.3 \text{ kJ}$$

Example 4: 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 $\Delta H = mC\Delta T$.

$$C = 4.18 \text{ J/(g} \cdot \text{°C)}$$

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

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

$$\Delta H = ?$$

$$\Delta H = mC\Delta T$$

$$\Delta H = (100.0 \text{ g})(4.18 \text{ J/(g} \cdot \text{°C)})(60.0^\circ\text{C}) = 25080 \text{ J}$$

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

Example 5: 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).

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

$$n = \frac{18.02 \text{ g}}{18.0158 \text{ g/mol}}$$

$$n = 1.000233129 \text{ mol H}_2\text{O}$$

$$C_{\text{water}} = 4.18 \text{ kJ/(kg} \cdot \text{°C)}$$

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

$$\Delta H_{\text{vap}} = 40.65 \text{ kJ/mol}$$

$$C_{\text{steam}} = 2.02 \text{ kJ/(kg} \cdot \text{°C)}$$

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

$$\Delta H = ?$$

$$\Delta H = mC_w\Delta T_w + n\Delta H_{\text{vap}} + mC_s\Delta T_s$$

(water) (vaporization) (steam)

$$\Delta H = (0.01802 \text{ kg})(4.18 \text{ kJ/(kg} \cdot \text{°C)})(20.0^\circ\text{C}) +$$

$$(1.000233129 \text{ mol})(40.65 \text{ kJ/mol}) +$$

$$(0.01802 \text{ kg})(2.02 \text{ kJ/(kg} \cdot \text{°C)})(15^\circ\text{C})$$

$$\Delta H = 1.506472 \text{ kJ} + 40.65947669 \text{ kJ} + 0.546006 \text{ kJ}$$

$$\Delta H = 42.7 \text{ kJ}$$

- Calorimetry:** - uses the conservation of energy (**Heat Gained = Heat Lost**) to measure calories (old unit of heat: 1 cal = 4.18 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 6: Hot water at 90.0°C is poured into 100 g of cold water at 10.0°C. The final temperature of the mixture is 70.0°C. Determine the mass of the hot water?

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

$$C = 4.18 \text{ J/(g} \cdot \text{°C)}$$

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

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

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

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

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

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

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

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

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

Example 7: A 1500 g of iron metal at 330°C is dropped into a beaker of 1000 g of water at 25.0°C. What will be the final temperature?

$$T_f = ?$$

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

$$C_{\text{Fe}} = 0.449 \text{ J/(g} \cdot \text{°C)}$$

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

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

$$C_{\text{water}} = 4.18 \text{ J/(g} \cdot \text{°C)}$$

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

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

(iron, kinetic) (water, kinetic)

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

$$(1500 \text{ g})(0.449 \text{ J/(g} \cdot \text{°C)})(330^\circ\text{C} - T_f) = (1000 \text{ g})(4.18 \text{ J/(g} \cdot \text{°C)})(T_f - 25.0^\circ\text{C})$$

$$222255 - 673.5T_f = 4180T_f - 104500$$

$$-673.5T_f - 4180T_f = -104500 - 222255$$

$$-4853.5T_f = -326755$$

$$T_f = \frac{-326755}{-4853.5}$$

$$T_f = 67.3^\circ\text{C}$$

Assignment

6.1 pg. 281 #21 to 28

6.2 pg. 504–505 #81 to 86; pg. 280 #9, 10; pg. 281–282 #29 to 44

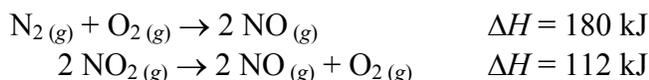
6.3: Hess's Law

Hess's Law: - the **addition of ΔH** of a series of reactions to find the change in enthalpy of an overall net reaction.

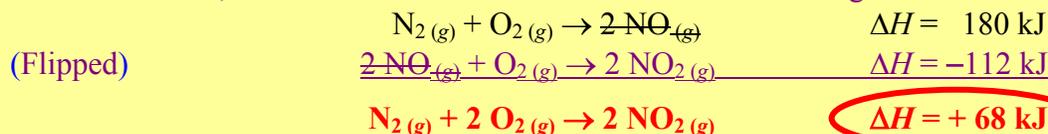
- when adding reactions, **compared the reactants and products of the overall net reaction with the intermediate reactions given. Decide on the intermediate reactions that need to be reversed or multiply by a coefficient or both, such that when added, the intermediate products will cancel out perfectly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

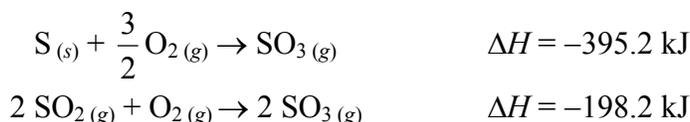
Example 1: Calculate ΔH for the reaction $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$, when the following reactions are given.



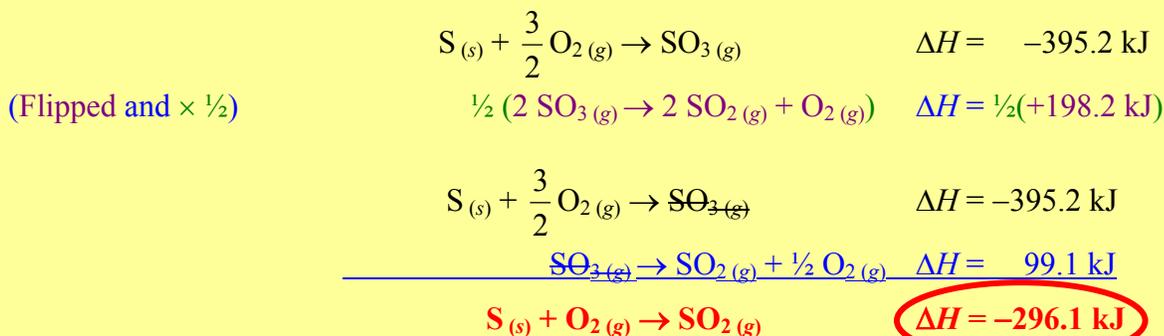
Note that 2 NO_2 in the net reaction is on the product side, whereas 2 NO_2 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH .



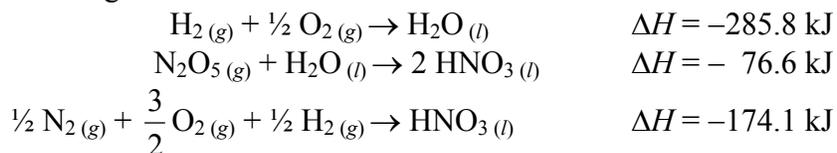
Example 2: Determine the ΔH for the reaction $\text{S}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$, when the following reactions are given.



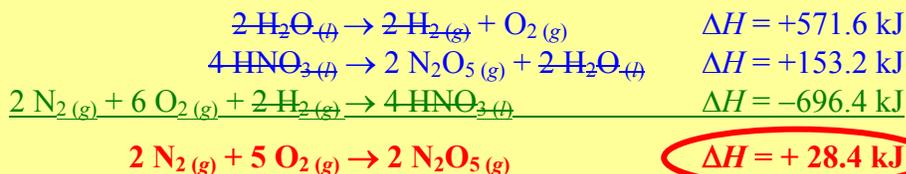
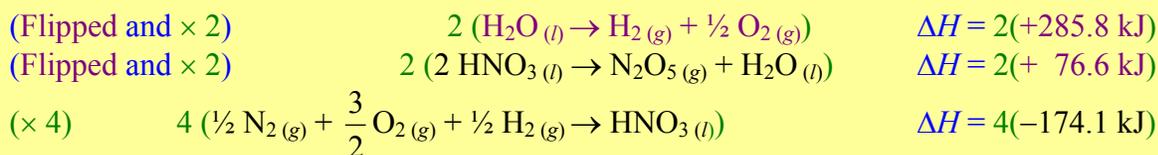
- SO_2 in the net reaction is on the product side, whereas 2 SO_2 in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the ΔH .
- There is only 1 SO_2 in the net reaction, whereas there are 2 SO_2 in the second reaction. Therefore the second reaction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



Example 3: Find the ΔH 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 .
- 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 need to be multiplied by the coefficient of 2.
- There are 2N_2 in the net 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 by the coefficient of 4.
- In order for H_2O to cancel from the first and second reactions, we have to multiply 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.



6.4: Standard Enthalpies of Formation

- Molar Heat of Formation (ΔH_f):** - the amount of heat required / given off to make 1 mole of compound from its elemental components.
- the **Molar Heat of Formation of ALL ELEMENTS is 0 kJ.**
 - the **state of the compound affects the magnitude of H_f .**
($\text{H}_2\text{O}(\text{g})$ has $H_f = -241.8 \text{ kJ/mol}$; $\text{H}_2\text{O}(\text{l})$ has $H_f = -285.8 \text{ kJ/mol}$)
 - **Standard Molar Heat of Formation (H°_f)** is the heat of formation under standard conditions (1 atm and 25°C).

(See Appendix Four on pg. A21 to A23 in the Zumdahl 6th ed. Chemistry textbook for a list of H°_f)

Enthalpy of Formation (Chemical)

$$\Delta H = n\Delta H_f$$

ΔH = Change in Enthalpy n = moles
 ΔH_f = Molar Heat of Formation (kJ/mol)

Example 1: Find the molar heat of formation of table salt given that $2 \text{Na}_{(s)} + \text{Cl}_{2(g)} \rightarrow 2 \text{NaCl}_{(s)} + 822 \text{kJ}$.

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

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

$$\Delta H_f = ?$$

$$\Delta H = n\Delta H_f$$

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

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

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 $\Delta H_f = -393.5 \text{ kJ/mol}$)?

$$n = \frac{100 \text{ g}}{44.011 \text{ g/mol}}$$

$$n = 2.272159233 \text{ mol NaCl}$$

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

$$\Delta H = ?$$

$$\Delta H = n\Delta H_f$$

$$\Delta H = (2.272159233 \text{ mol})(-393.5 \text{ kJ/mol})$$

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

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 ($\Delta H_f = -826 \text{ kJ/mol}$ for Fe_2O_3)?

$$\Delta H = 1.20 \text{ MJ} = -1.20 \times 10^3 \text{ kJ}$$

$$\Delta H_f = -826 \text{ kJ/mol}$$

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

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

$$\Delta H = n\Delta H_f$$

$$n = \frac{\Delta H}{\Delta H_f} = \frac{-1.20 \times 10^3 \text{ kJ}}{-826 \text{ kJ/mol}} = 1.452784504 \text{ mol}$$

$$m = nM = (1.455957292 \text{ mol})(159.7 \text{ g/mol})$$

$$m = 232 \text{ g}$$

Example 4: Calculate the molar heat 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.

$$n = \frac{91.2 \text{ g}}{231.74 \text{ g/mol}}$$

$$n = 0.3935444895 \text{ mol Ag}_2\text{O}$$

$$\Delta H = -12.2 \text{ kJ}$$

$$\Delta H_f = ?$$

$$\Delta H = n\Delta H_f$$

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

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

Molar Enthalpy of Reaction: - the amount of heat involved when 1 mol of a particular product is produced or 1 mol of a particular reactant is consumed.

- it is equal to the difference between of all enthalpies of products and all enthalpies of reactants.

- if the reaction is a **combustion**, it is called the molar heat of combustion.

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

Theoretical Enthalpy of Reaction

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

ΔH_{rxn} = Change in Enthalpy of Reaction

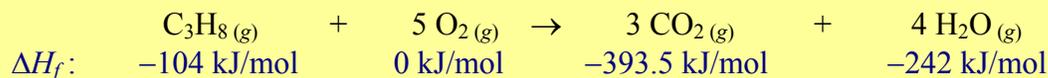
$\Sigma H_{\text{products}}$ = Sum of Heat of Products (from all $n\Delta H_f$ of products)

$\Sigma H_{\text{reactants}}$ = Sum of Heat of Reactants (from all $n\Delta H_f$ of reactants)

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

- Calculate the ΔH of combustion of propane.
- Draw its potential energy diagram.
- 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.



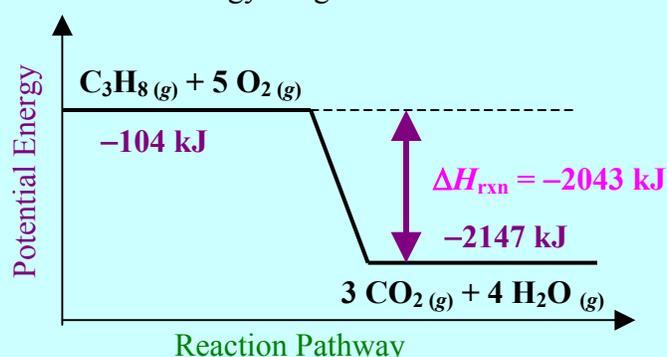
$$\Delta H_{\text{rxn}} = \Sigma H_{\text{products}} - \Sigma H_{\text{reactants}}$$

$$\Delta H_{\text{rxn}} = [3 \text{ mol} (-393.5 \text{ kJ/mol}) + 4 \text{ mol} (-242 \text{ kJ/mol})] - [1 \text{ mol} (-104 \text{ kJ/mol}) + 5 \text{ mol} (0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = [-2147 \text{ kJ}] - [-104 \text{ kJ}]$$

$$\Delta H_{\text{rxn}} = -2043 \text{ kJ/mol of C}_3\text{H}_8 \text{ burned}$$

b. Potential Energy Diagram



c. From part a., for every 1 mol of C_3H_8 burned, 2043.9 kJ is released.

$$n = \frac{15.0 \text{ g}}{44.0962 \text{ g/mol}} = 0.3401653657 \text{ mol C}_3\text{H}_8$$

$$\Delta H_{\text{rxn}} = -2043 \text{ kJ/mol}$$

$$\Delta H = ?$$

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

$$\Delta H = (0.3401653657 \text{ mol})(-2043 \text{ kJ/mol})$$

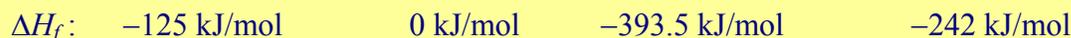
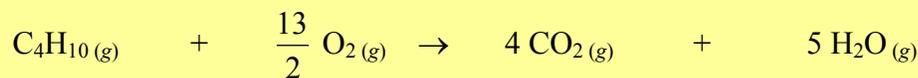
$$\Delta H = -695 \text{ kJ} \quad (695 \text{ kJ is released})$$

Example 6: Determine the amount of heat released when 34.9 g of butane gas is burned ($\Delta H_f = -125 \text{ kJ/mol}$ for butane).

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.)



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

$$\Delta H_{\text{rxn}} = [4 \text{ mol} (-393.5 \text{ kJ/mol}) + 5 \text{ mol} (-242 \text{ kJ/mol})] - [1 \text{ mol} (-125 \text{ kJ/mol}) + \frac{13}{2} \text{ mol} (0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = [-2784 \text{ kJ}] - [-125 \text{ kJ}]$$

$$\Delta H_{\text{rxn}} = -2659 \text{ kJ/mol of C}_4\text{H}_{10} \text{ burned}$$

$$n = \frac{34.9 \text{ g}}{58.123 \text{ g/mol}} = 0.6004507682 \text{ mol C}_4\text{H}_{10}$$

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

$$\Delta H = (0.6004507682 \text{ mol})(-2659 \text{ kJ/mol}) = -1596.599 \text{ kJ}$$

$$\Delta H_{\text{rxn}} = -2659 \text{ kJ/mol}$$

$$\Delta H = ?$$

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

Chemical Calorimetry

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

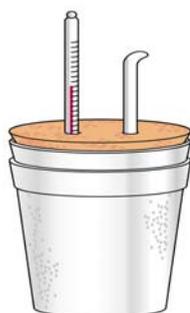
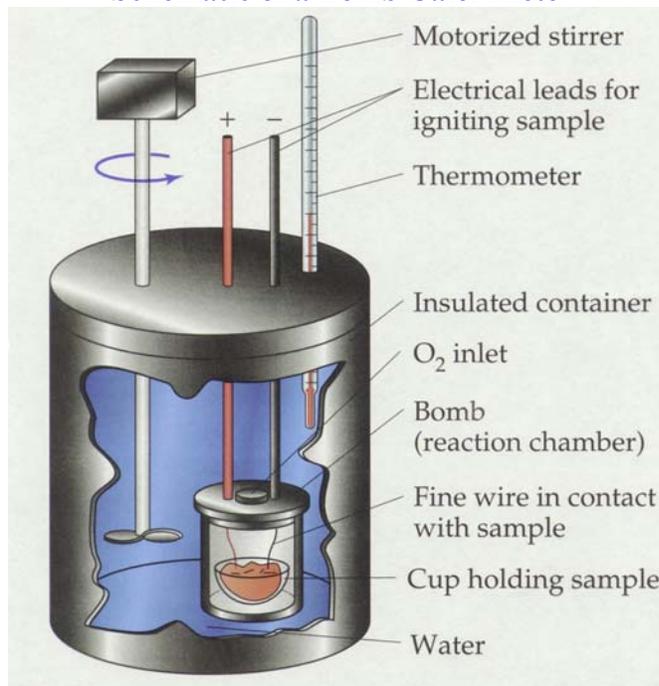
$$n\Delta H_{\text{rxn}} = mC\Delta T$$

or

$$n\Delta H_{\text{sol}} = mC\Delta T$$

(Check out Calorimetry Animation at
<http://web.umn.edu/~gbert/animation.html>)

A Simple Calorimeter

**Schematic of a Bomb Calorimeter**

- 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. Ignore the metallic material of the calorimeter,
- determine the experimental molar heat of combustion heptane.
 - find the theoretical molar heat of combustion of heptane ($\Delta H_f = -188$ kJ/mol for heptane).
 - explain why the experimental ΔH is different than its theoretical counterpart.

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

$$n = \frac{10.02 \text{ g}}{100.2034 \text{ g/mol}}$$

$$n = 0.0999966069 \text{ mol C}_7\text{H}_{16}$$

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

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

$$C_{\text{water}} = 4.18 \text{ kJ / (kg} \cdot ^\circ\text{C)}$$

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

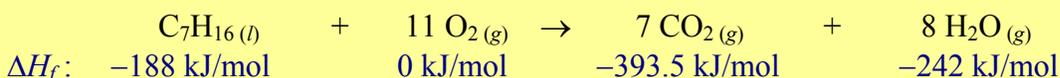
$$n\Delta H_{\text{rxn}} = m_w C_w \Delta T$$

$$\Delta H_{\text{rxn}} = \frac{m_w C_w \Delta T}{n} = \frac{(1.50 \text{ kg})(4.18 \text{ kJ/(kg} \cdot ^\circ\text{C)})(65.0^\circ\text{C})}{(0.0999966069 \text{ mol})}$$

$$\Delta H_{\text{rxn}} = 4075.63829 \text{ kJ/mol (released)}$$

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

b. To find theoretical ΔH_{rxn} for the combustion of heptane, we have to use Hess's Law.



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

$$\Delta H_{\text{rxn}} = [7 \text{ mol}(-393.5 \text{ kJ/mol}) + 8 \text{ mol}(-242 \text{ kJ/mol})] - [1 \text{ mol}(-188 \text{ kJ/mol}) + 11 \text{ mol}(0 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = [-4690.5 \text{ kJ}] - [-188 \text{ kJ}] = -4502.5 \text{ kJ}$$

$$\text{Theoretical } \Delta H_{\text{rxn}} = -4.50 \text{ MJ/mol of C}_7\text{H}_{16} \text{ burned}$$

- c. Some of the possible reasons why experimental ΔH_{rxn} (-4.08 MJ) is different than the theoretical ΔH_{rxn} (-4.50 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: $\text{HCOOH}_{(g)}$ were completely burned to $\text{CO}_2_{(g)}$ and $\text{H}_2\text{O}_{(l)}$ in a calorimeter. The following are the observation of the experiment.

Mass of $\text{HCOOH}_{(g)}$ burned	9.22 g
Initial Temperature of Calorimeter and Water	21.5°C
Final Temperature of Calorimeter and Water	37.3°C
Specific Heat of Calorimeter and Water	3.20 kJ/°C

- a. Determine the experimental molar heat of formation of $\text{HCOOH}_{(l)}$.
- b. If the theoretical ΔH_f for $\text{HCOOH}_{(g)}$ is -363 kJ/mol, calculate the % error of this experiment.

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

$$n = \frac{9.22 \text{ g}}{46.0268 \text{ g/mol}}$$

$$n = 0.2003180756 \text{ mol HCOOH}$$

$$m_{\text{water}} \cdot C_{\text{water}} = 3.20 \text{ kJ/}^\circ\text{C}$$

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

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

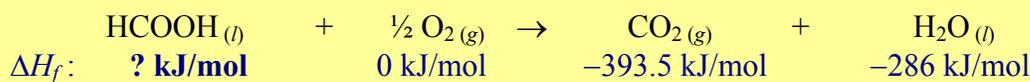
$$n\Delta H_{\text{rxn}} = m_w C_w \Delta T$$

$$\Delta H_{\text{rxn}} = \frac{m_w C_w \Delta T}{n} = \frac{(3.20 \text{ kJ/}^\circ\text{C})(15.8^\circ\text{C})}{(0.2003180756 \text{ mol})}$$

$$\Delta H_{\text{rxn}} = 252.3985908 \text{ kJ/mol (released)}$$

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

Next, we use Hess's Law to find the ΔH_f of HCOOH .



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

$$-252 \text{ kJ} = [1 \text{ mol} (-393.5 \text{ kJ/mol}) + 1 \text{ mol} (-286 \text{ kJ/mol})] - [1 \text{ mol} (\Delta H_f) + \frac{1}{2} \text{ mol} (0 \text{ kJ/mol})]$$

$$-252 \text{ kJ} = [-679.5 \text{ kJ}] - [\Delta H_f]$$

$$\Delta H_f = -679.5 \text{ kJ} + 252 \text{ kJ} = -427.5 \text{ kJ}$$

$$\text{Experimental HCOOH } \Delta H_f = -428 \text{ kJ/mol}$$

$$\text{b. \% error} = \left| \frac{\text{Theoretical} - \text{Experimental}}{\text{Theoretical}} \right| \times 100\% = \left| \frac{(-363 \text{ kJ}) - (-428 \text{ kJ})}{(-363 \text{ kJ})} \right| \times 100\% \quad \text{\% error} = 17.9\%$$

Assignment

6.3 pg. 283 #51 to 58 6.4 pg. 284 #59 to 68; pg. 282–283 #45 to 50

6.5: Present Sources of Energy

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

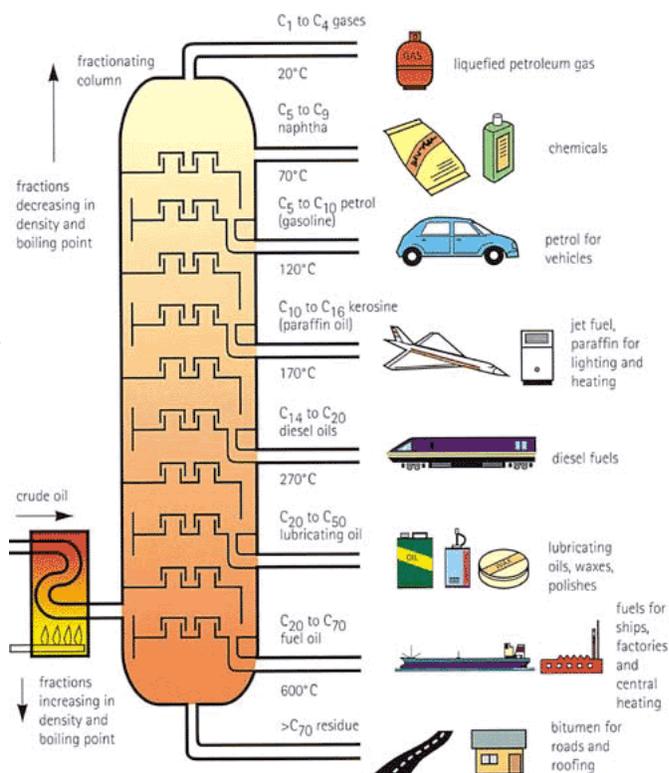
Incomplete Combustion: - where the main product of combustion is carbon monoxide, along with carbon dioxide and water vapour.
- happens when carbon particles started to form during combustion and deposited as soot as they cooled, or when there is insufficient oxygen.
- characterized by a yellow flame.

Example: Incomplete combustion of Propane.
$$\text{C}_3\text{H}_8(\text{g}) + 4 \text{O}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g}) + \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{g})$$

- 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.

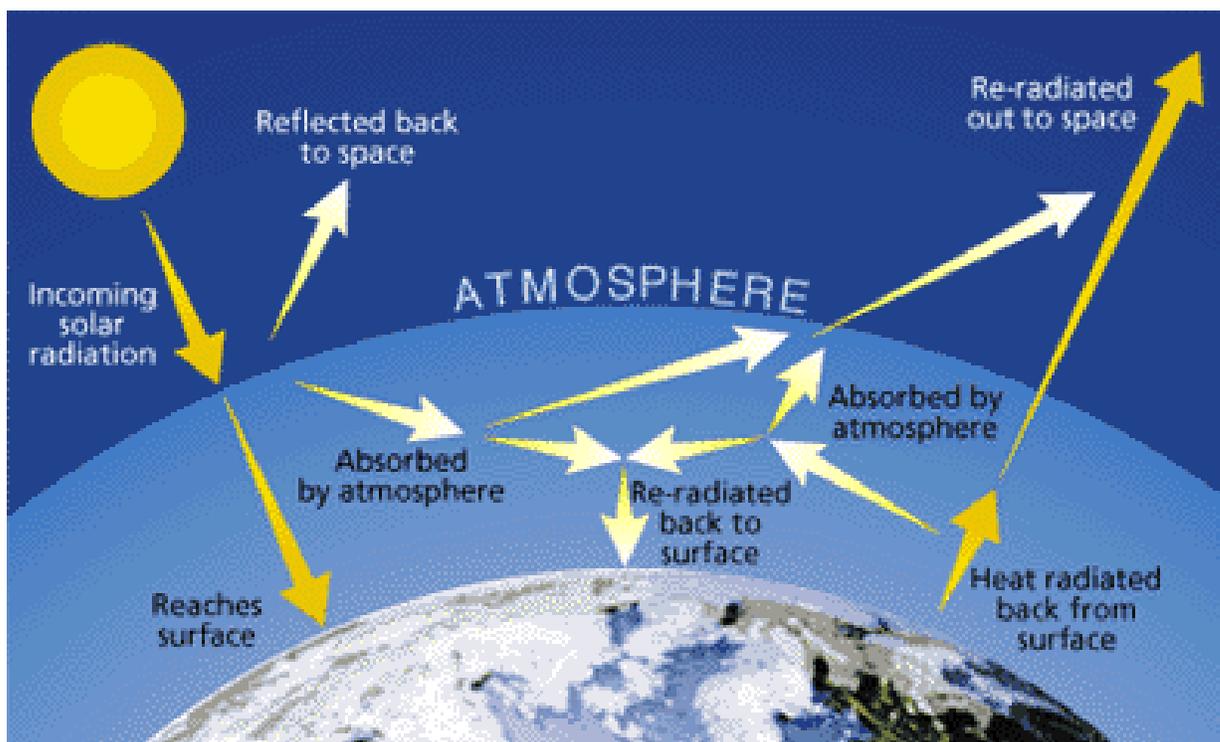
Example: The Cracking of Hexadecane.
$$\text{C}_{16}\text{H}_{34} + 2 \text{H}_2 \xrightarrow{\text{catalyst and heat}} \text{C}_8\text{H}_{18} + \text{C}_8\text{H}_{18}$$

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 (CO₂)** is released to the atmosphere when solid waste, fossil fuels (oil, natural gas, and coal), and wood and wood products are burned.
2. **Methane (CH₄)** 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 (N₂O)** 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.

6.6: New Energy Sources

Alternate Energy Sources without the Emission of Greenhouse Gas

- 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.
- 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 landscapes.
- Geothermal Power**: - the use of underground steam to generate electricity.
 - very efficient somewhat 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.
- Tidal Power**: - the use of tidal current to generate electricity.
 - very efficient somewhat reliable, but location specific.
 - tidal power involves establishing 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.
- 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.
- 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.

Assignment

6.6 pg. 284–285 #69 to 74

Chapter 16: Spontaneity, Entropy and Free Energy**16.1: Spontaneous Process and Entropy**

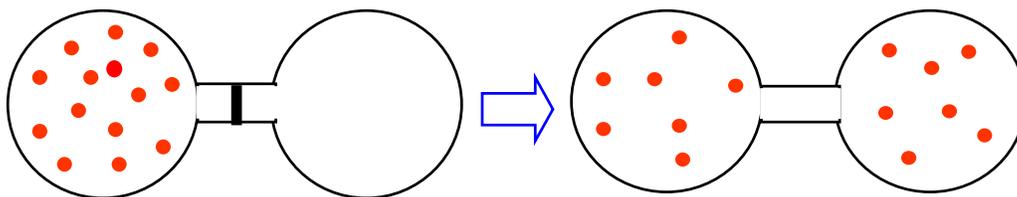
Spontaneous Process: - a thermodynamic process that happens without any external interventions.
 - it does NOT indicate the speed (kinetics) of the process.

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

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

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

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



Open valve: gas spontaneously expands

More probable state (Entropy increases)



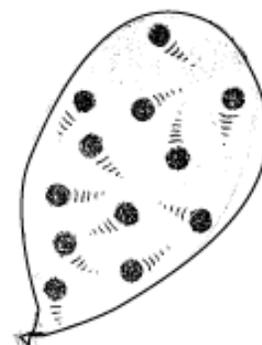
S_{solid}

<



S_{liquid}

<<



S_{gas}

Example 1: For the following process, determine whether it is spontaneous and predict the sign of ΔS .

- the heat from the heat vent eventually warms up the room.
- diluting a salt solution.
- photosynthesis occurs naturally in plants

a. the heat from the heat vent eventually warms up the room.

(**Spontaneous**, $\Delta S > 0$, temperature naturally goes from high to low to achieve thermodynamic equilibrium)

b. diluting a salt solution.

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

c. photosynthesis occurs naturally in plants.

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

16.2: Entropy and the Second Law of Thermodynamics

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

Second Law of Thermodynamics

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

When $\Delta S_{\text{univ}} > 0$, the process is **Thermodynamically Spontaneous**

When $\Delta S_{\text{univ}} = 0$, the **System is at Equilibrium** ($\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$)

When $\Delta S_{\text{univ}} < 0$, the process is **Thermodynamically Non-Spontaneous**

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

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

Assignment

16.1 pg. 819 #15 to 17; 19, 20

16.2 pg. 818 #9 and 11

16.3: The Effect of Temperature on Spontaneity

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

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

ΔS_{surr} = Entropy of the Surrounding (kJ/K)

ΔH = Change in Enthalpy of the Process (kJ) T = Temperature (K)

When $\Delta H < 0$, $\Delta S_{\text{surr}} > 0$

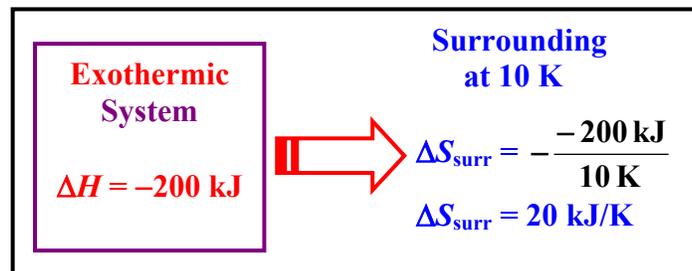
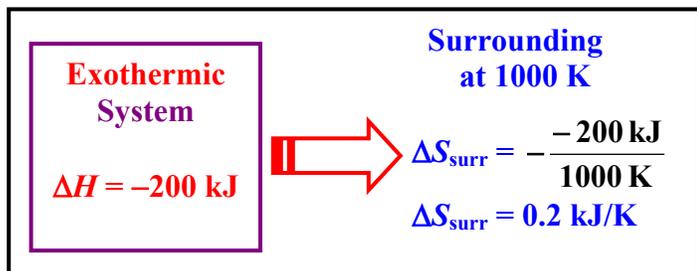
When $\Delta H > 0$, $\Delta S_{\text{surr}} < 0$

When T is Large, $|\Delta S_{\text{surr}}|$ is Small

When T is small, $|\Delta S_{\text{surr}}|$ is Large

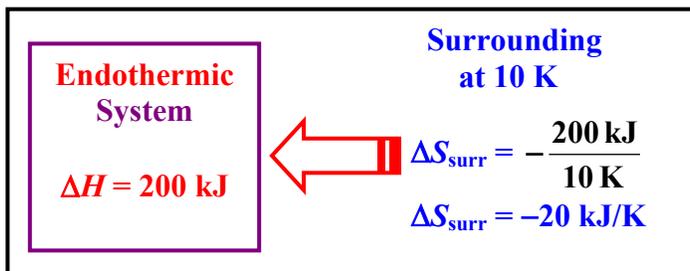
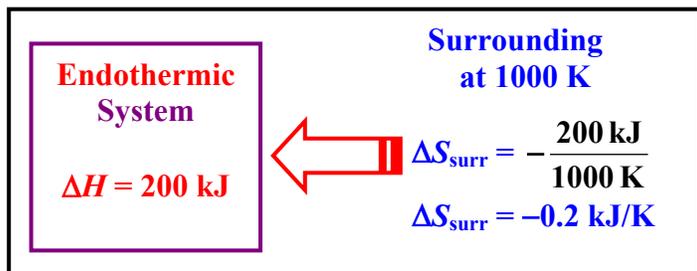
1. **System is Exothermic** ($\Delta H < 0$): $-\Delta S_{\text{surr}} > 0$ (Surrounding's Randomness Increases – Less Order)

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



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

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



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

Example 1: The molar heat of fusion for water is 6.01 kJ/mol. Determine the ΔS_{surr} for the following phase change of $\text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)}$ at -20.0°C and at 10.0°C under 1 atm.

$$\begin{array}{l} \Delta H = 6.01 \text{ kJ/mol} \\ T_1 = -20.0^\circ\text{C} = 253.15 \text{ K} \\ T_2 = 10.0^\circ\text{C} = 283.15 \text{ K} \end{array} \quad \begin{array}{c} \text{H}_2\text{O}_{(s)} \rightarrow \text{H}_2\text{O}_{(l)} \\ \Delta S_{\text{surr}} = -\frac{\Delta H}{T_1} = -\frac{6.01 \text{ kJ}}{253.15 \text{ K}} \end{array} \quad \begin{array}{l} \Delta H = 6.01 \text{ kJ} \\ \Delta S_{\text{surr}} = -\frac{\Delta H}{T_2} = -\frac{6.01 \text{ kJ}}{283.15 \text{ K}} \end{array}$$

$$\Delta S_{\text{surr}} = ?$$

$$\begin{array}{l} \Delta S_{\text{surr}} = -2.37 \times 10^{-2} \text{ kJ/K at } -20.0^\circ\text{C} \\ \Delta S_{\text{surr}} = -23.7 \text{ J/K at } -20.0^\circ\text{C} \end{array} \quad \begin{array}{l} \Delta S_{\text{surr}} = -2.12 \times 10^{-2} \text{ kJ/K at } 10.0^\circ\text{C} \\ \Delta S_{\text{surr}} = -21.2 \text{ J/K at } 10.0^\circ\text{C} \end{array}$$

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

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

$$\begin{array}{l} \Delta H = -393.5 \text{ kJ/mol} \\ T_1 = -40.0^\circ\text{C} = 233.15 \text{ K} \\ T_2 = 40.0^\circ\text{C} = 313.15 \text{ K} \end{array} \quad \begin{array}{c} \text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} \\ \Delta S_{\text{surr}} = -\frac{\Delta H}{T_1} = -\frac{-393.5 \text{ kJ}}{233.15 \text{ K}} \end{array} \quad \begin{array}{l} \Delta H = -393.5 \text{ kJ} \\ \Delta S_{\text{surr}} = -\frac{\Delta H}{T_2} = -\frac{-393.5 \text{ kJ}}{313.15 \text{ K}} \end{array}$$

$$\Delta S_{\text{surr}} = ?$$

$$\Delta S_{\text{surr}} = 1.69 \text{ kJ/K at } -40.0^\circ\text{C}$$

$$\Delta S_{\text{surr}} = 1.26 \text{ kJ/K at } 40.0^\circ\text{C}$$

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

16.4: Free Energy

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

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

$$\begin{array}{l} \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \\ \left(-\frac{\Delta G}{T}\right) = \Delta S^\circ + \left(-\frac{\Delta H^\circ}{T}\right) \end{array} \quad \begin{array}{l} (\Delta S_{\text{sys}} = \Delta S^\circ - \text{standard entropy at constant temperature and pressure}) \\ (\text{Substitute } \Delta S_{\text{univ}} \text{ with } -\frac{\Delta G}{T} \text{ and } \Delta S_{\text{surr}} \text{ with } -\frac{\Delta H^\circ}{T}) \end{array}$$

$$\begin{array}{l} T\left(-\frac{\Delta G}{T}\right) = T\Delta S^\circ + T\left(-\frac{\Delta H^\circ}{T}\right) \\ -\Delta G = T\Delta S^\circ - \Delta H^\circ \end{array} \quad \begin{array}{l} (\text{Multiply each term by } T) \\ (\text{Simplify and rearrange to } \Delta G = \Delta H^\circ - T\Delta S^\circ) \end{array}$$

Free Energy

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

$$\Delta G = \Delta H^\circ - T\Delta S^\circ$$

ΔG = Free Energy of the Universe (kJ/mol or J/mol)

ΔH = Enthalpy of the System (kJ/mol or J/mol) T = Temperature (K)

ΔS° = Standard Entropy the System (kJ/(K • mol) or J/(K • mol))

When $\Delta S_{\text{univ}} > 0$, $\Delta G < 0$, the process is **Thermodynamically Spontaneous**

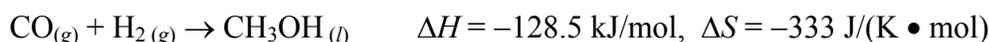
When $\Delta S_{\text{univ}} = 0$, $\Delta G = 0$, the System is at **Equilibrium** ($\Delta H^\circ = T\Delta S^\circ$)

When $\Delta S_{\text{univ}} < 0$, $\Delta G > 0$, the process is **Thermodynamically Non-Spontaneous**

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

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

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



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

a.

$$\Delta H = -128.5 \text{ kJ/mol}$$

$$\Delta S = -333 \text{ J/(K} \cdot \text{mol)} = -0.333 \text{ kJ/(K} \cdot \text{mol)}$$

$$T = 30.0^\circ\text{C} = 303.15 \text{ K}$$

$$\Delta G = ?$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G = (-128 \text{ kJ/mol}) - (303.15 \text{ K})(-0.333 \text{ kJ/(K} \cdot \text{mol)})$$

$$\Delta G = -27.1 \text{ kJ/mol at } 30.0^\circ\text{C}$$

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

b.

$$\Delta G = 0 \text{ at equilibrium}$$

$$\Delta H = -128.5 \text{ kJ/mol}$$

$$\Delta S = -0.333 \text{ kJ/(K} \cdot \text{mol)}$$

$$T = ?$$

$$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad 0 = \Delta H^\circ - T\Delta S^\circ \text{ at equilibrium}$$

$$T\Delta S^\circ = \Delta H^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-128 \text{ kJ/mol}}{-0.333 \text{ kJ/(K} \cdot \text{mol)}} = 384.384 \text{ K}$$

$$T_{\text{eq}} = 111^\circ\text{C}$$

c. At $T > 111^\circ\text{C}$, $\Delta G > 0$ because $-T\Delta S$ term will be **dominant** (bigger magnitude than ΔH°). The reaction will be **Non-Spontaneous**.

At $T < 111^\circ\text{C}$, $\Delta G < 0$ because ΔH° term will be **dominant** (bigger magnitude than $-T\Delta S$). The reaction will be **Spontaneous**.

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

$\Delta G = 0$ at boiling point

$\Delta H = 35.2$ kJ/mol

$\Delta S = 104$ J/(K • mol)

$\Delta S = 0.104$ kJ/(K • mol)

$T = ?$

$\text{CH}_3\text{OH}_{(l)} \rightarrow \text{CH}_3\text{OH}_{(g)} \quad \Delta H = 35.2 \text{ kJ/mol}, \Delta S = 104 \text{ J/(K} \cdot \text{mol)}$

$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad 0 = \Delta H^\circ - T\Delta S^\circ$ at equilibrium

$T\Delta S^\circ = \Delta H^\circ$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{35.2 \text{ kJ/mol}}{0.104 \text{ kJ/(K} \cdot \text{mol)}} = 338.4615 \text{ K}$$

Theoretical $T_b = 65.3^\circ\text{C}$

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

% error = 1.68%

Assignment

16.3 pg. 819 #21 and 22

16.4 pg. 819 #23 to 28

16.5: Entropy Changes in Chemical Reactions

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

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

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

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

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

ΔS° = Standard Change in Entropy of a System

$\sum S^\circ_{\text{products}}$ = Total Standard Entropy of all Products

$\sum S^\circ_{\text{reactants}}$ = Total Standard Entropy of all Reactants

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

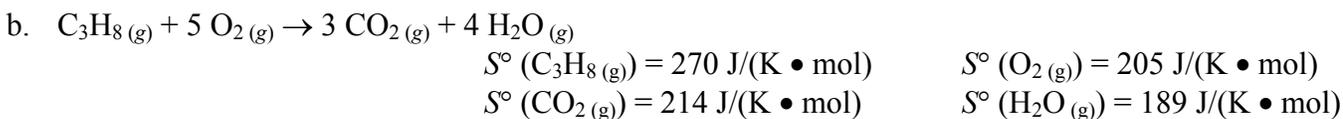


This is a phase change from gas to liquid, $\Delta S^\circ < 0$.

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = (1 \text{ mol})(70 \text{ J/(K} \cdot \text{mol)}) - (1 \text{ mol})(189 \text{ J/(K} \cdot \text{mol)})$$

$$\Delta S^\circ = -119 \text{ J/K (per mole of steam changed to water)}$$



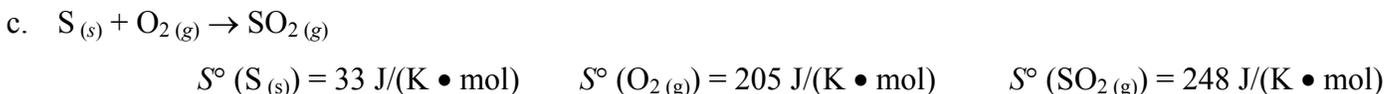
Since there are more moles of gaseous products, $\Delta S^\circ > 0$.

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

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

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

$$\Delta S^\circ = 103 \text{ J/K (per mole of propane burned)}$$



There is the same number of moles of gaseous chemicals on both sides of the equation. However, $\text{SO}_2_{(g)}$ has more bonds than $\text{O}_2_{(g)}$. Hence $\Delta S^\circ > 0$.

$$\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(1 \text{ mol})(248 \text{ J/(K} \cdot \text{mol)})] - [(1 \text{ mol})(205 \text{ J/(K} \cdot \text{mol)}) + (1 \text{ mol})(33 \text{ J/(K} \cdot \text{mol)})]$$

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

$$\Delta S^\circ = 10 \text{ J/K (per mole of SO}_2_{(g)} \text{ formed)}$$

16.6: Free Energy and Chemical ReactionsFree Energy of a Chemical Reaction

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{or} \quad \Delta G^\circ = \Sigma G^\circ_{\text{products}} - \Sigma G^\circ_{\text{reactants}}$$

ΔG° = Standard Change in Free Energy of a System

$\Sigma G^\circ_{\text{products}}$ = Total Standard Free Energy of all Products

$\Sigma G^\circ_{\text{reactants}}$ = Total Standard Free Energy of all Reactants

Example 1: Given that $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{g})$ has a $\Delta H = -484 \text{ kJ}$ and $\Delta S = -89.0 \text{ J/K}$, determine the free energy for ΔG° of the given chemical equation at 25.0°C .

$$\Delta H = -484 \text{ kJ}$$

$$\Delta S = -89.0 \text{ J/K} = -0.0890 \text{ kJ/K}$$

$$T = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G = ?$$



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

$$\Delta G = -457 \text{ kJ at } 25.0^\circ\text{C}$$

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

Example 2: Given that $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ has the following thermodynamic values, determine ΔH° , ΔS° and ΔG° of the given chemical equation at 25.0°C . At what temperature will the formation of ammonia at equilibrium?

Chemicals	H° (kJ/mol)	S° [J/(K • mol)]
$\text{N}_2(\text{g})$	0	192
$\text{H}_2(\text{g})$	0	131
$\text{NH}_3(\text{g})$	-46	193

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

$$\Delta H^\circ = [(2 \text{ mol})(-46 \text{ kJ/mol})] - [(1 \text{ mol})(0 \text{ kJ/mol}) + (3 \text{ mol})(0 \text{ kJ/mol})] = -92 \text{ kJ}$$

$$\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$$

$$\Delta S^\circ = [(2 \text{ mol})(193 \text{ J/(K • mol)})] - [(1 \text{ mol})(192 \text{ J/(K • mol)}) + (3 \text{ mol})(131 \text{ J/(K • mol)})]$$

$$\Delta S^\circ = [386 \text{ J/K}] - [585 \text{ J/K}] = -199 \text{ J/K}$$

$$\Delta H = -92 \text{ kJ}$$

$$\Delta S = -199 \text{ J/K} = -0.199 \text{ kJ/K}$$

$$T = 25.0^\circ\text{C} = 298.15 \text{ K}$$

$$\Delta G = ? \quad T_{\text{eq}} = ?$$



$$\Delta G = \Delta H^\circ - T\Delta S^\circ = (-92 \text{ kJ}) - (298.15 \text{ K})(-0.199 \text{ kJ/K})$$

$$\Delta G = -33 \text{ kJ at } 25.0^\circ\text{C}$$

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

$$\Delta G = \Delta H^\circ - T\Delta S^\circ \quad 0 = \Delta H^\circ - T\Delta S^\circ \text{ at equilibrium}$$

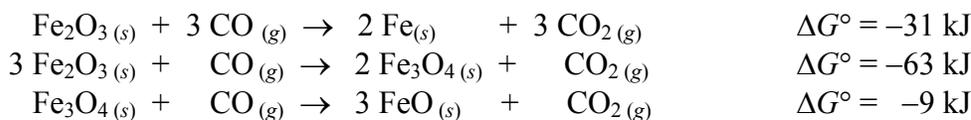
$$T\Delta S^\circ = \Delta H^\circ$$

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{-92 \text{ kJ}}{-0.199 \text{ kJ/K}} = 462.312 \text{ K}$$

$$T_{\text{eq}} = 169^\circ\text{C}$$

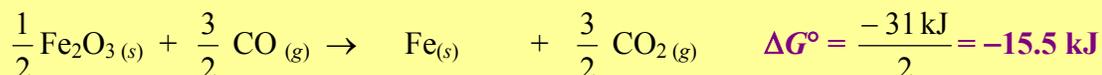
For the reaction to go forward, T must be kept below 169°C .

Example 3: Given the following data,

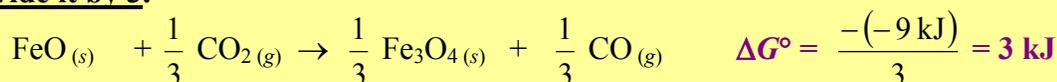


calculate the ΔG° for the reaction $\text{FeO}(s) + \text{CO}(g) \rightarrow \text{Fe}(s) + \text{CO}_2(g)$

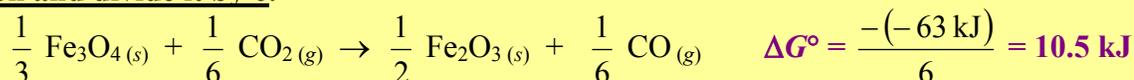
Since 1 mole of $\text{Fe}(s)$ is found on the product side of the final equation, we must divide the 1st equation by 2.



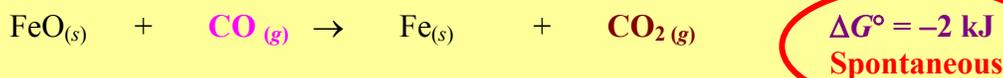
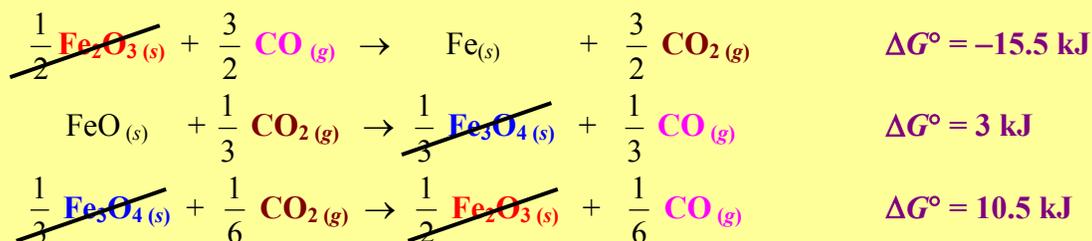
Because 1 mole of $\text{FeO}(s)$ is located at the reactant side of the final equation, we must flip the 3rd equation and divide it by 3.



Now we have to cancel out $\frac{1}{2}$ mole of $\text{Fe}_2\text{O}_3(s)$ from the modified 1st equation. Hence, we must flip the 2nd equation and divide it by 6.



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



$(\frac{3}{2} \text{CO}(g) - (\frac{1}{3} \text{CO}(g) + \frac{1}{6} \text{CO}(g))$ yields 1 $\text{CO}(g)$ on the reactant side)

$(\frac{3}{2} \text{CO}_2(g) - (\frac{1}{3} \text{CO}_2(g) + \frac{1}{6} \text{CO}_2(g))$ yields 1 $\text{CO}_2(g)$ on the product side)

Assignment

16.5 pg. 819–820 #29 to 40

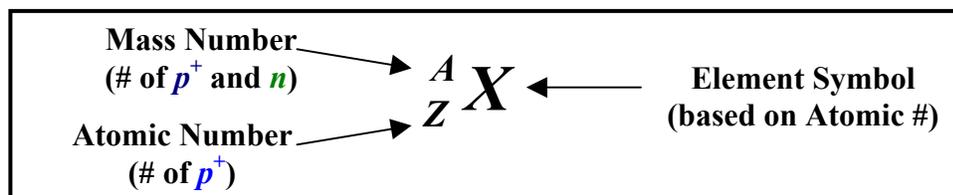
16.6 pg. 820 #41 to 50

Chapter 18: The Nucleus: A Chemist's View18.1: Nuclear Stability and Radioactive Decay

Nucleons: - the particles that make up a nucleus of an atom (protons, p^+ and neutrons, n).

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

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



Thermodynamic Stability: - amount of potential energy inside a nucleus versus total potential energy of all nucleons.

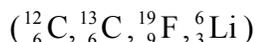
- the difference in energy can be calculated using Einstein's equation ($\Delta E = \Delta mc^2$), where Δm is referred to as mass defect.

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

Common Observations of Radioactive Decay

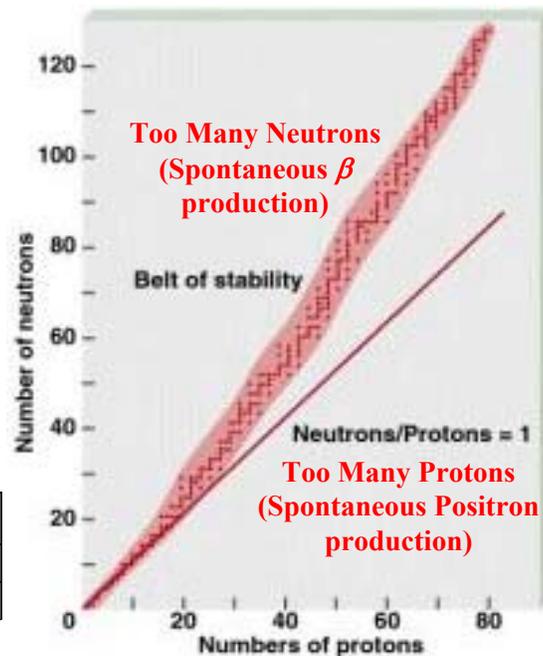
- When a nuclide has 84 or more protons ($Z \geq 84$), it tends to be **unstable** and likely undergo **radioactive decay**.
- Lighter nuclides are stable when $A = n$ (or $n : p^+$ ratio = 1). However, heavier nuclides are stable only when $A < n$ (or $n : p^+$ ratio > 1).
- Nuclides with **even # of 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_3Li
# of p^+	6 (even)	6 (even)	9 (odd)	3 (odd)
# of n	6 (even)	7 (odd)	10 (even)	3 (odd)

Stability: Most \longrightarrow Least



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

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.

Types of Radioactive Decay

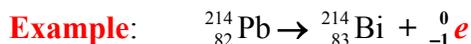
1. **Alpha Particle (α particle)**: - basically a helium nucleus (${}^4_2\text{He}$), commonly found during radioactive decay from heavier nuclide (the net result is to increase the neutron to proton ratio).



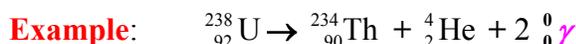
Spontaneous Fission: - when a heavy nuclide splits into two lighter nuclides and sometimes neutrons.



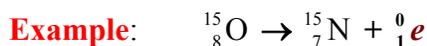
2. **Beta Particle (β particle)**: - basically an electron (${}^0_{-1}\text{e}$) that is emitted when the neutron to proton ratio is higher than the zone of stability (**a neutron is transformed to a proton become the net result**).
- electrons have a mass number of 0 and an atomic number assignment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



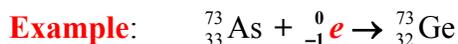
3. **Gamma Ray (γ ray)**: - also known as a high-energy photon (${}^0_0\gamma$) that is usually a by-product of an alpha-particle decay.
- photon has no mass and no atomic number.



4. **Positron (e^+)**: - an antimatter of electron (${}^0_1\text{e}$) that is emitted when the neutron to proton ratio is lower than the zone of stability (a proton is transformed to a neutron become the net result).
- positrons have a mass number of 0 and an atomic number assignment of 1, due to its charge.
 - when a positron and an electron collide, they **annihilate** themselves to produce energy (**matter-antimatter reaction**).



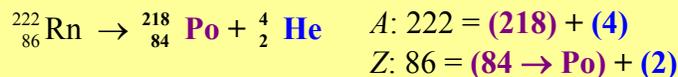
5. **Electron Capture**: - an inner-orbital electron is “captured” by the nucleus to increase neutron to proton ratio. It is usually accompanied by an emission of gamma ray.



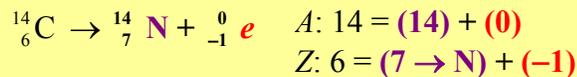
Balancing Nuclear Equations: - the total atomic number (Z) and the total atomic mass (A) have to balance on both sides.

Example 1: Balance the following nuclear equations.

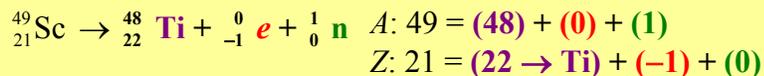
a. $^{222}_{86}\text{Rn}$ produces an α particle.



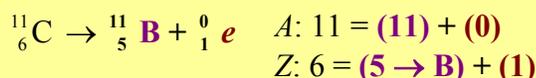
b. $^{14}_6\text{C}$ produces a β particle.



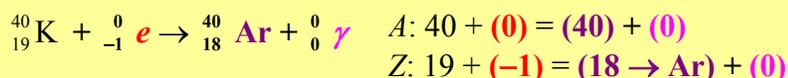
c. $^{49}_{21}\text{Sc}$ produces a β particle and a neutron.



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



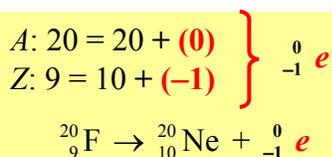
e. $^{40}_{19}\text{K}$ captures an electron to produce γ ray



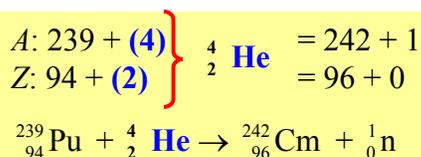
f. ^1_1H reacts with $^{15}_7\text{N}$ to produce an α particle with γ ray.



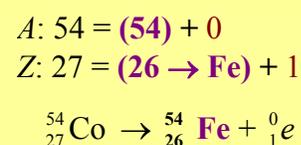
g. $^{20}_9\text{F} \rightarrow ^{20}_{10}\text{Ne} + \underline{\hspace{2cm}}$



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



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

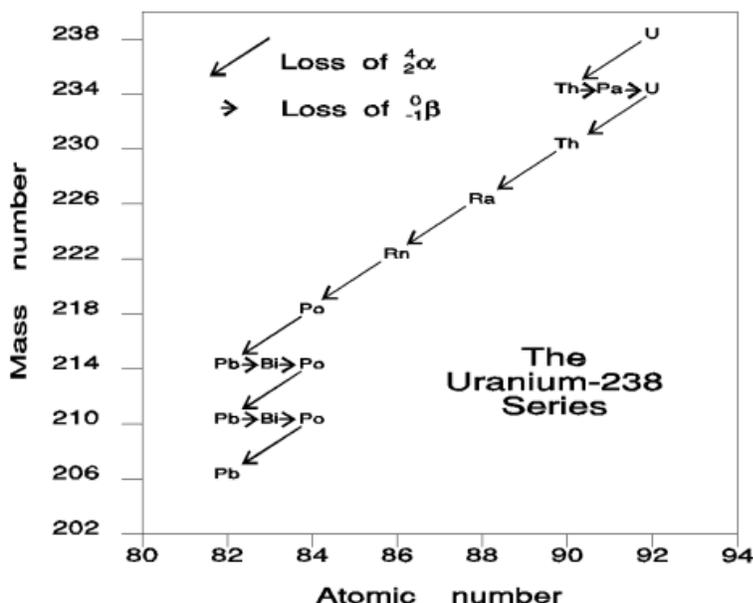


18.2: The Kinetics of Radioactive Decay

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).



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

$$\frac{1}{N} \Delta N = -k \Delta t \quad (\text{Rearrange Equation for Integration})$$

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

$$\ln N - \ln N_0 = -kt \quad (\text{Apply one of the Logarithm Laws: } \log A - \log B = \log \left(\frac{A}{B} \right))$$

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

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 $\frac{1}{2} N_0 = N$:

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

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

Radioactive Decay Equations

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

N = Amount of Nuclide at time t

N_0 = Amount of Nuclide at time 0

k = Rate Constant

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?

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

$N = ?$

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

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

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

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

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

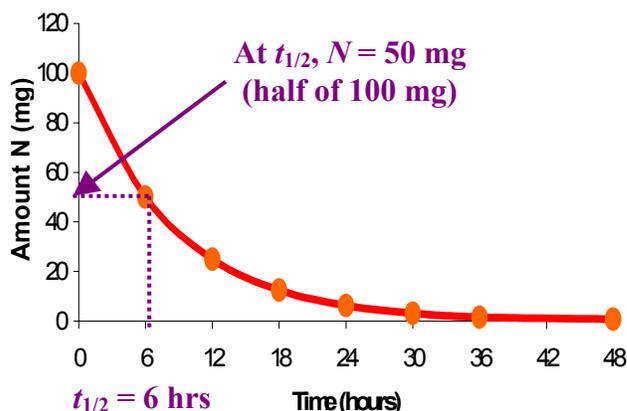
$$\ln \left(\frac{N}{N_0} \right) = -kt \quad \frac{N}{N_0} = e^{-kt}$$

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

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

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

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 :

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

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

Assignment

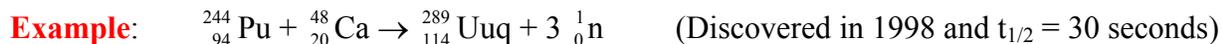
18.1 pg. 906–907 #9 to 12, 14

18.2 pg. 907 #19 to 26

18.3: Nuclear Transformations

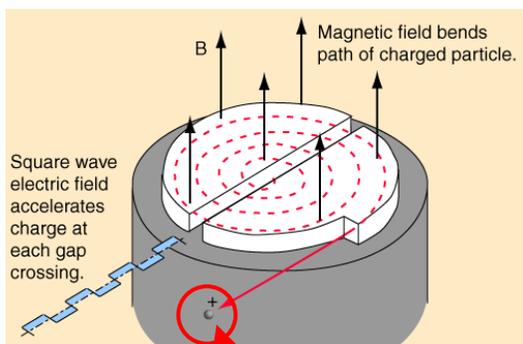
Nuclear Transformation: - the reaction where one element is converted to another element by changing the number of protons.
 - also refer to as **transmutation**.

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.

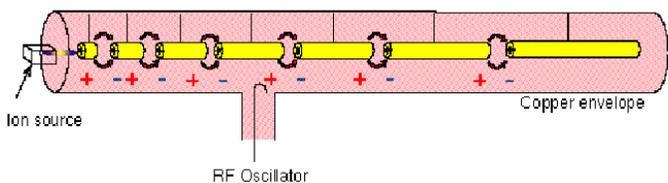
a. **Cyclotron:** - a type of particle accelerator that utilizes a changing electric field along with a magnetic field to increase the speed of an ion around a disc before hitting a target nuclide.



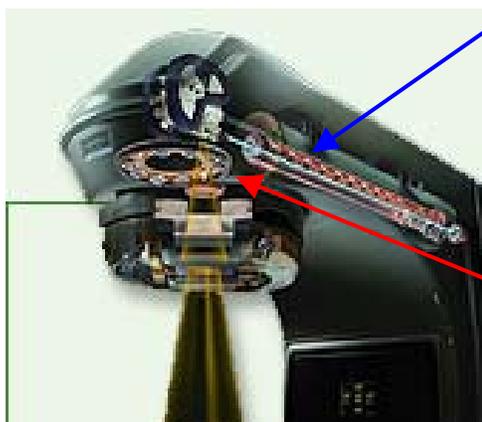
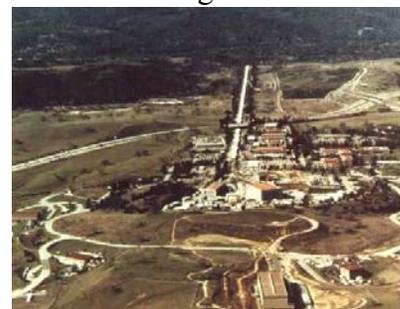
COMET: A medical superconducting cyclotron. It is used to generate thallium-201 (coronary arteries) and gallium-67 (soft-tissue tumors). It can also produce radio-pharmaceutical needed for PET and SPECT scans

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.



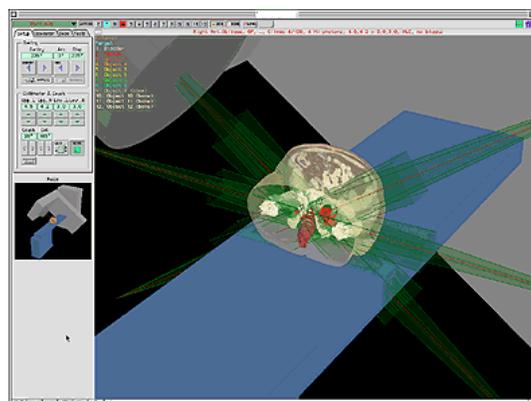
Left: Schematic of a Linear Accelerator
 Right: Stanford Linear Accelerator



Linear Accelerator

Multileaf Collimator to shape the beam

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

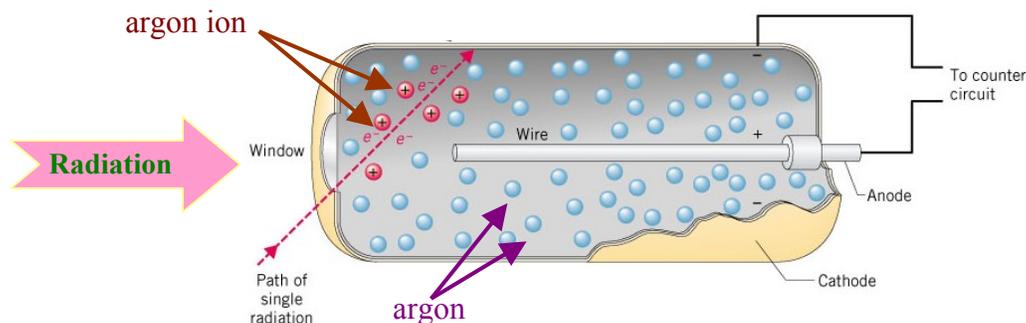


Schematic of a Medical Linear Accelerator

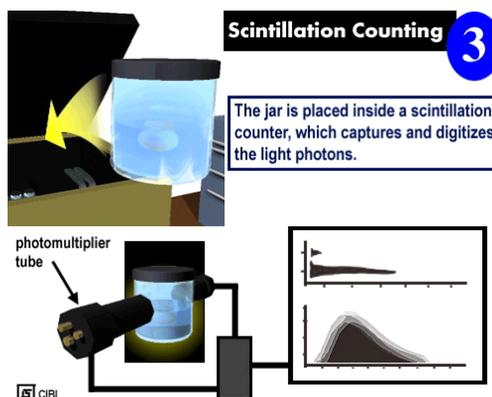
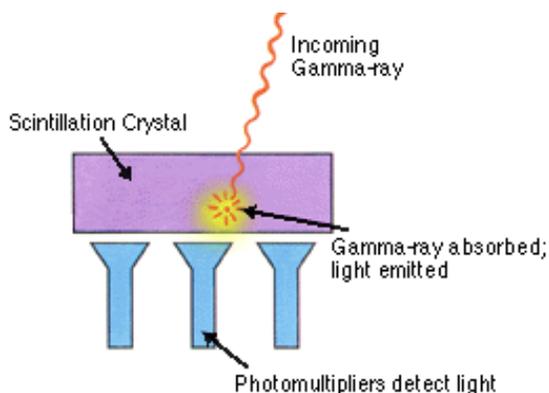
18.4: Detection and Uses of Radioactivity

Geiger-Müller Counter: - sometimes refer to as the **Geiger Counter**.

- 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.



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



Radiocarbon Dating: - sometimes called **carbon-14 dating**. $^{14}_6\text{C}$ can be found naturally in organic material and the atmosphere. It decays as soon as the organism dies ($^{14}_6\text{C} \rightarrow ^0_{-1}e + ^{14}_7\text{N}$).

- uses the known ratio of $^{14}_6\text{C}/^{12}_6\text{C}$ of similar organic sample of the day with the ratio in the artifact and the half-life of $^{14}_6\text{C}$ being 5730 years to determine the age of the artifact.

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

Example 1: An ancient wooden artifact 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 artifact.

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

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 .

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

Example 2: A piece of ore containing $^{238}_{92}\text{U}$ and $^{206}_{82}\text{Pb}$ was found. The ratio between $^{206}_{82}\text{Pb}$ to $^{238}_{92}\text{U}$ is 0.432. Suppose that no $^{206}_{82}\text{Pb}$ was originally present. Determine the age of the ore given that the half-life of $^{238}_{92}\text{U}$ is 4.5×10^9 years.

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

$$t_{1/2} = 4.5 \times 10^9 \text{ yrs} \quad t = ?$$

First, we solve for k .

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

Next, we solve for t .

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

Assignment

18.3 pg. 907 #17 and 18

18.4 pg. 907–908 #27 to 30

18.5: Thermodynamic Stability of the Nucleus

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**,
 $1 \text{ amu} = 1.66 \times 10^{-27} \text{ kg}$).

Subatomic Particle	Mass (kg)	Atomic Mass Unit (amu)
Neutron	1.67493×10^{-27}	1.00899
Proton	1.67262×10^{-27}	1.00760
Electron	9.10939×10^{-31}	5.48758×10^{-4}

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.
 - when the amount of energy is small, we convert the unit to **electron volt**
 ($1 \text{ eV} = 1.69 \times 10^{-19} \text{ J}$ or $1 \text{ MeV} = 1.69 \times 10^{-13} \text{ J}$).

Albert Einstein's Mass-Energy Conversion

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

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

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

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

$$m \text{ of } (6p^+, 7n \text{ and } 6e^-) = 6(1.00760 \text{ amu}) + 7(1.00899 \text{ amu}) + 6(5.48758 \times 10^{-4} \text{ amu}) = 13.11182255 \text{ amu}$$

$$\Delta m = m \text{ of } {}^{13}_6\text{C} - m \text{ of } (6p^+, 7n \text{ and } 6e^-) = 13.003355 \text{ amu} - 13.11182255 \text{ amu} \quad \Delta m = -0.108467548 \text{ amu}$$

$$\Delta E = -\Delta mc^2 = -(-0.108467548 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})(3.00 \times 10^8 \text{ m/s})^2 = 1.62 \times 10^{-11} \text{ J}$$

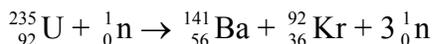
$$\Delta E_{\text{bind per nucleon}} = \frac{1.62 \times 10^{-11} \text{ J}}{13 \text{ nucleons}}$$

$$\Delta E_{\text{bind}} = 1.25 \times 10^{-12} \text{ J/nucleon}$$

$$\Delta E_{\text{bind}} = 1.25 \times 10^{-12} \text{ J/nucleon} \times \frac{1 \text{ MeV}}{1.69 \times 10^{-13} \text{ J}}$$

$$\Delta E_{\text{bind}} = 7.38 \text{ MeV/nucleon}$$

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



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

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

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

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

$$\Delta E = -\Delta mc^2 = -(-0.18532 \text{ amu})(1.66 \times 10^{-27} \text{ kg/amu})(3.00 \times 10^8 \text{ m/s})^2 = 2.7686808 \times 10^{-11} \text{ J/nucleus}$$

$$\Delta E_{\text{bind}} = 2.7686808 \times 10^{-11} \text{ J/nucleus} \times (6.022 \times 10^{23} \text{ nucleus/mol}) = 1.67 \times 10^{13} \text{ J/mol}$$

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

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

18.6: Nuclear Fission and Nuclear Fusion

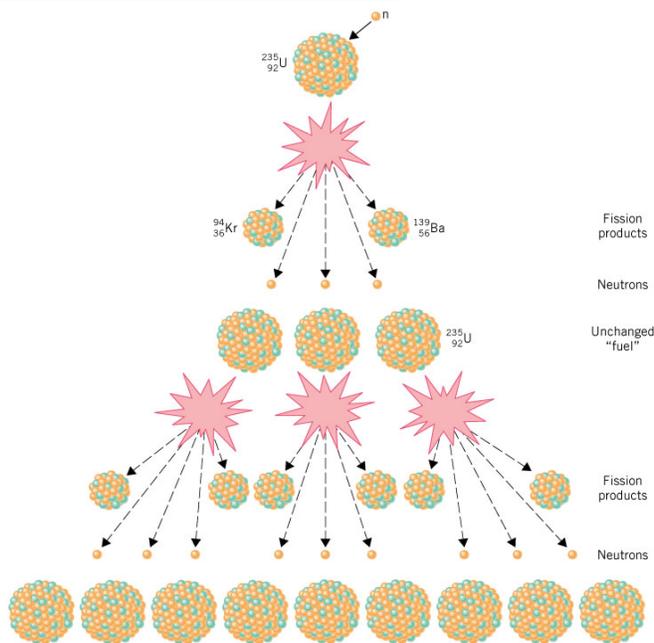
Nuclear Fission: - the breaking up of a heavier nucleus into two nuclei with small mass number.



(See Animation at <http://reactor.engr.wisc.edu/fission.htm>)

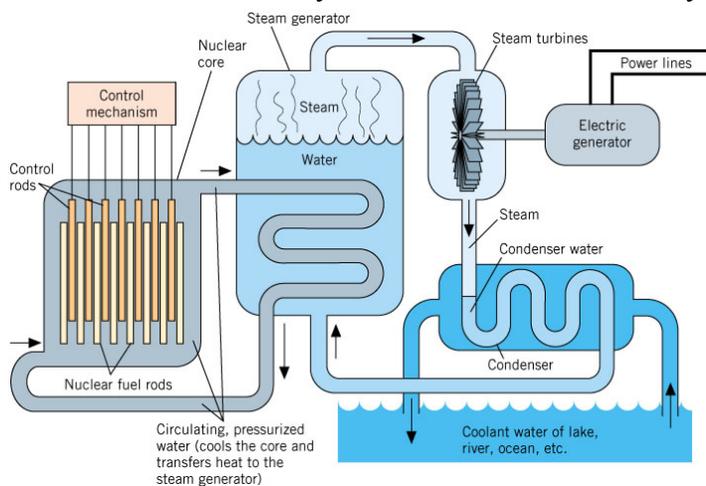
Chain Reaction: - when the nuclear fission is self-sustaining.

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



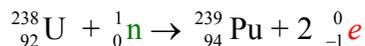
Nuclear Reactors: - fission reactors where enriched ${}_{92}^{235}\text{U}$ is placed in the **reactor core (nuclear core)**, **control rods (usually made of carbon to absorb extra neutrons)** can be lifted or lowered to control the rate of the fission process. As the water of the surrounding is heated, it transferred the heat to a steam generator to generate electricity via a steam turbine. The water is then cooled and recycled.

- the by-products of ${}_{92}^{235}\text{U}$ 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

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.

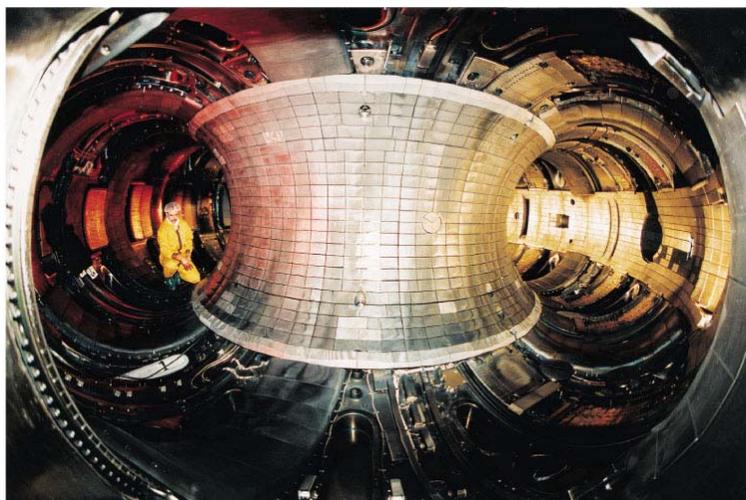


Nuclear Fusion: - the combining of two light nuclei into a heavier and more stable nucleus.

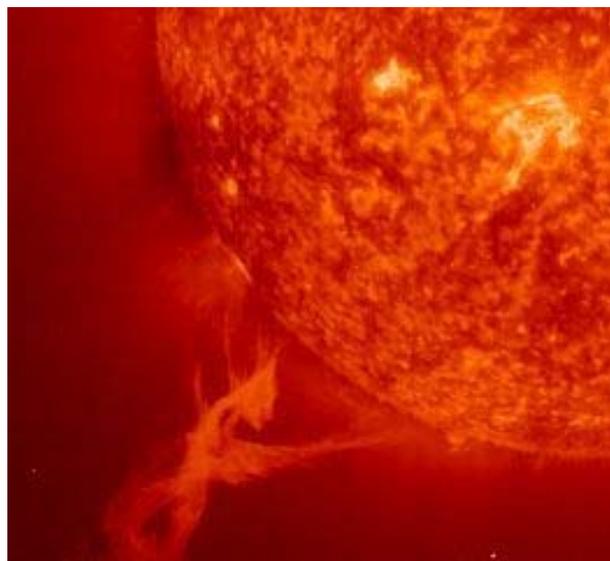


(See Animation at <http://reactor.engr.wisc.edu/fission.htm>)

- 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 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.



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.



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

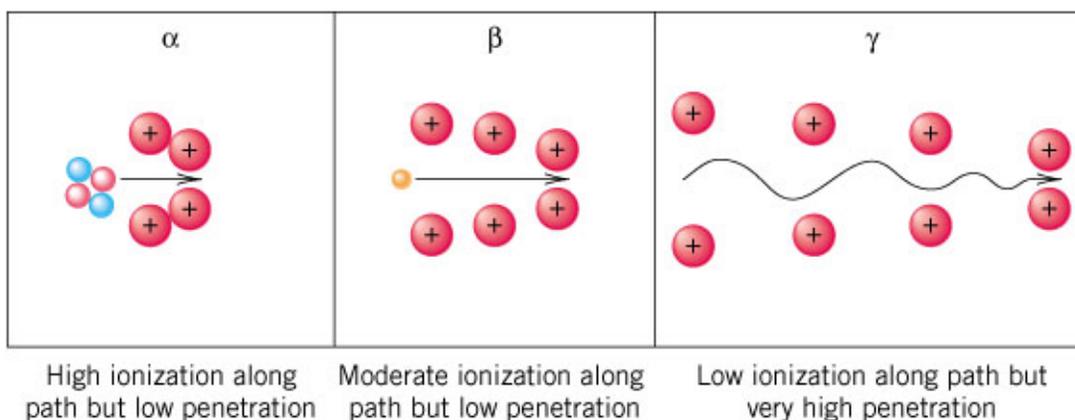
18.7: Effects of Radiation

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.

- Somatic Damages:** - radiation damages to the organism's tissues or cell structures that cause sickness or death.
- Genetic Damages:** - radiation damages to the genetic code or reproduction process of the organism, which causes mutations in the offspring.

Biological Effects from Radiation

- Radiation Energy Level:** - the higher the energy levels (doses), the more the severe are the damages.
 - the radiation doses are measured in *rads* (radiation absorbed doses), where 1 rad = 10 mJ.
- Penetrating Ability:** - the lighter the particles, the more penetrating they can be. In terms of penetrating ability: **γ ray is the strongest, follows by β particles and α particle is the least penetrating.**
- Ionization Ability:** - as high-energy particles pass through tissue, it can cause ionization that is damaging to the organism. **α particles can 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** 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**18.5 pg. 908 #31 to 38****18.7 pg. 909 #43 and 49**