

## Unit 4: THERMOCHEMISTRY AND NUCLEAR CHEMISTRY

### Chapter 6: Thermochemistry

#### 6.1: The Nature of Energy and Types of Energy

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

##### Different Types of Energy:

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

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

#### 6.2: Energy Changes in Chemical Reactions

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

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

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

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

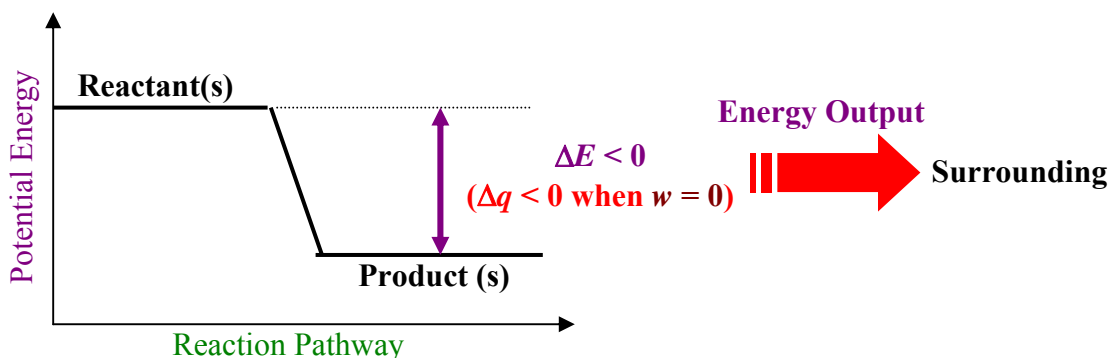
**Open System:** - a system where **mass and energy can interchange** freely with its surrounding.

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

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

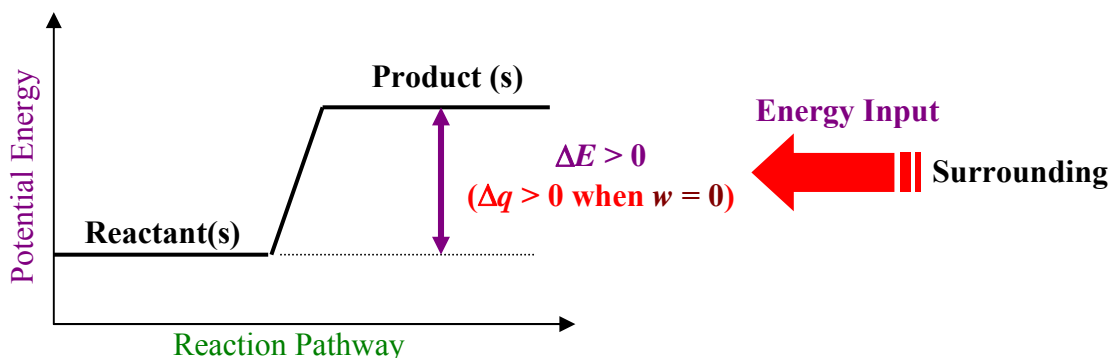
**Exothermic Process** ( $\Delta E < 0$ ): - when energy flows “out” of the system into the surrounding.  
(Surrounding gets Warmer.)

**Potential Energy Diagram for Exothermic Process**



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

**Potential Energy Diagram for Endothermic Process**



### **6.3: Introduction of Thermodynamics**

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

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

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

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

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

$$\Delta E = q + w$$

$\Delta E$  = 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**).

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

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

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

$$w = -P \Delta V$$

(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.

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

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

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

$$\Delta E = ?$$

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

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

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

### Assignment

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

**6.4: Enthalpy of Chemical Reactions**

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

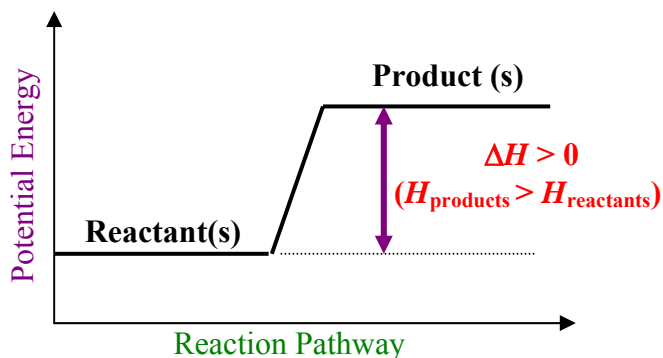
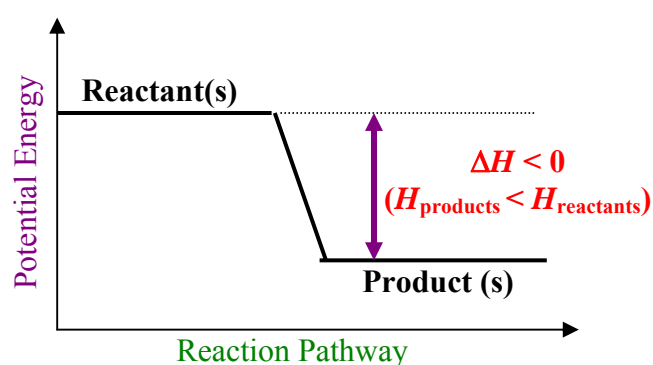
$$\begin{aligned} \Delta E &= q - P\Delta V & (\Delta E = \Delta H - P\Delta V \text{ Rearrange formula for enthalpy}) \\ \Delta H - P\Delta V &= q - P\Delta V & (\text{Equate } \Delta E \text{ and simplify by cancelling } -P\Delta V \text{ on both sides}) \\ \Delta H &= q & (\text{Change in Enthalpy is Change in Heat of a system at constant pressure and little change in volume.}) \end{aligned}$$

**Change in Enthalpy in a Chemical Reaction**

$$\begin{aligned} \Delta H &= q = H_{\text{products}} - H_{\text{reactants}} \\ \Delta H > 0 & \text{ Endothermic Reaction} \\ \Delta H < 0 & \text{ Exothermic Reaction} \end{aligned}$$

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

$$\begin{aligned} \Delta H &= \text{Change in Enthalpy} & n = \text{moles} \\ \Delta H_{\text{rxn}} &= \text{Molar Enthalpy of Reaction (kJ/mol)} \end{aligned}$$

**Potential Energy Diagram for Endothermic Chemical Reactions / Physical Processes****Potential Energy Diagram for Exothermic Chemical Reactions / Physical Processes****Writing ΔH Notations with Chemical Equations / Physical Process:****a. Endothermic Reactions / Processes**

**Example:** Water is vaporized from its liquid state.

**b. Exothermic Reactions / Processes**

**Example:** Methane undergoes combustion at constant pressure.



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

$$\begin{aligned} \Delta H &= 116.2 \text{ kJ} \\ V &= 84.0 \text{ L} \\ P &= 1.00 \text{ atm} \\ T &= 25.0^\circ\text{C} = 298.15 \text{ K} \\ R &= 0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}} \\ n &=? \quad \Delta H_{\text{rxn}} = ? \end{aligned} \quad n = \frac{PV}{RT} = \frac{(1.00 \text{ atm})(84.0 \text{ L})}{(0.0821 \frac{\text{atm}\cdot\text{L}}{\text{mol}\cdot\text{K}})(298.15 \text{ K})} = 3.431636791 \text{ mol}$$

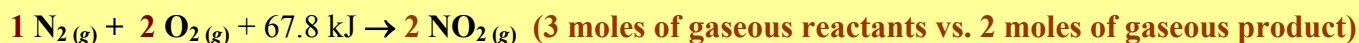
$$\Delta H = n\Delta H_{\text{rxn}} \quad \Delta H_{\text{rxn}} = \frac{\Delta H}{n} = \frac{116.2 \text{ kJ}}{3.431636791 \text{ mol}} \quad \Delta H_{\text{rxn}} = 33.9 \text{ kJ/mol}$$

$$\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g}) \quad \Delta H = 67.8 \text{ kJ} \quad (2 \text{ mol of NO}_2 \text{ in Eq})$$

$$\text{or } \frac{1}{2} \text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g}) \quad \Delta H = 33.9 \text{ kJ}$$

**Example 2:** Using the chemical equation from the last example,  $\text{N}_2(\text{g}) + 2 \text{O}_2(\text{g}) \rightarrow 2 \text{NO}_2(\text{g})$ , show mathematically that the enthalpy change is approximately the same as the total internal energy change when the system is kept at a constant pressure of 1.00 atm and  $25.0^\circ\text{C}$ .

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



$$\Delta E = q - P\Delta V \quad (\text{Using the Ideal Gas Law, substitute } P\Delta V = \Delta nRT)$$

$$\Delta E = q - \Delta nRT \quad (\text{Substitute values - using } R = 8.31 \text{ J}/(\text{K} \cdot \text{mol}))$$

$$\Delta E = 67.8 \text{ kJ} - (-1 \text{ mol})(8.31 \text{ J}/(\text{K} \cdot \text{mol}) \times \frac{1 \text{ kJ}}{1000 \text{ J}})(298.15 \text{ K})$$

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

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

**Example 3:** Given that  $2 \text{C}_4\text{H}_{10}(\text{g}) + 13 \text{O}_2(\text{g}) \rightarrow 8 \text{CO}_2(\text{g}) + 10 \text{H}_2\text{O}(\text{g}) + 5317 \text{ kJ}$ , calculate the change in enthalpy when 28.2 g of butane is burned.

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

$$n = \frac{28.2 \text{ g}}{58.14 \text{ g/mol}} \quad \Delta H = n\Delta H_{\text{rxn}} = (0.4850361197 \text{ mol})(-2658.5 \text{ kJ/mol})$$

$$n = 0.4850361197 \text{ mol C}_4\text{H}_{10}$$

$$\Delta H = ?$$

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

$$(1 \text{ MJ} = 1000 \text{ kJ})$$

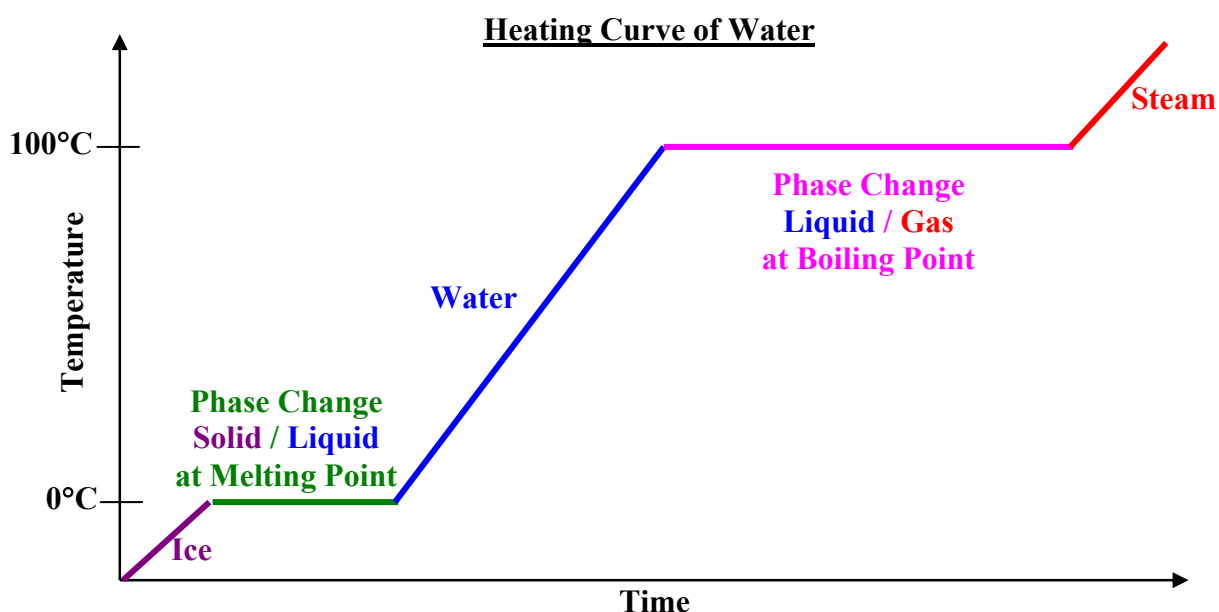
### Assignment

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

6.5 & 11.8: Calorimetry and Phase ChangesEnergy 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 ( $\Delta H_{\text{fus}}$ ):** - 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 ( $\Delta H_{\text{vap}}$ ):** - the amount of heat needed to evaporate one mole of substance from liquid to gas at its boiling point (in kJ/mol)

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

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

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

**Heat Capacity ( $C$ ):** - the amount of heat (J or kJ) needed to a given amount of substance by  $1^{\circ}\text{C}$  or 1 K.  
- usually used in a calorimeter (see section 6.5).

### Physical Potential Change

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

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

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

$q$  = Heat Change (J or kJ)

$n$  = moles

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

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

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

### Physical Kinetic Change

$$q = mc\Delta T$$

$$q = C\Delta T$$

$q$  = Heat Change (J or kJ)  $m$  = mass (g or kg)  $\Delta T$  = Change in Temperature (in  $^{\circ}\text{C}$  or K)

$c$  = Specific Heat [J/(g  $\cdot$   $^{\circ}\text{C}$ ) or kJ/(kg  $\cdot$   $^{\circ}\text{C}$ ) or J/(g  $\cdot$  K) or kJ/(kg  $\cdot$  K)]

$C$  = Heat Capacity [J/ $^{\circ}\text{C}$  or kJ/ $^{\circ}\text{C}$  or J/K or kJ/K]

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

Substance	Melting Point ( $^{\circ}\text{C}$ )	Boiling Point ( $^{\circ}\text{C}$ )	Specific Heat Capacity [kJ/(kg $\cdot$ $^{\circ}\text{C}$ )]	$\Delta H_{\text{fus}}$ (kJ/mol)	$\Delta H_{\text{vap}}$ (kJ/mol)
Ice $\text{H}_2\text{O}_{(s)}$	0	----	2.03	6.01	----
Water $\text{H}_2\text{O}_{(l)}$	----	100	4.184	----	40.79
Steam $\text{H}_2\text{O}_{(g)}$	----	----	1.99	----	----
Ammonia $\text{NH}_3_{(g)}$	-77.73	-33.34	2.06	5.66	23.33
Methanol $\text{CH}_3\text{OH}_{(l)}$	-98	64.6	2.53	3.22	35.21
Ethanol $\text{C}_2\text{H}_5\text{OH}_{(l)}$	-114.1	78.3	2.46	7.61	39.3
Aluminum $\text{Al}_{(s)}$	660	2519	0.900	10.79	294
Carbon (graphite) $\text{C}_{(s)}$	3338	4489	0.720	117	----
Copper $\text{Cu}_{(s)}$	1085	2562	0.385	12.93	300.4
Iron $\text{Fe}_{(s)}$	1538	2861	0.444	13.81	340
Mercury $\text{Hg}_{(l)}$	-39	357	0.139	23.4	59.0

**Example 1:** What is the change in enthalpy involved when 36.04 g of water boils from liquid to gas at  $100^{\circ}\text{C}$ ?

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

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

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

$$q = ?$$

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

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

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

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

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

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

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

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

$$q = ?$$

$$q = mc\Delta T$$

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

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

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

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

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

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

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

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

$$q = ?$$

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

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

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

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

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

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

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

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

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

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

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

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

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

$$q_{\text{total}} = mc_w\Delta T_w + n\Delta H_{\text{vap}} + mc_s\Delta T_s$$

(water)      (vaporization)      (steam)

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$$T_f = ?$$

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

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

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

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

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

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

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

$$-4850T_f = -324380$$

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

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

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

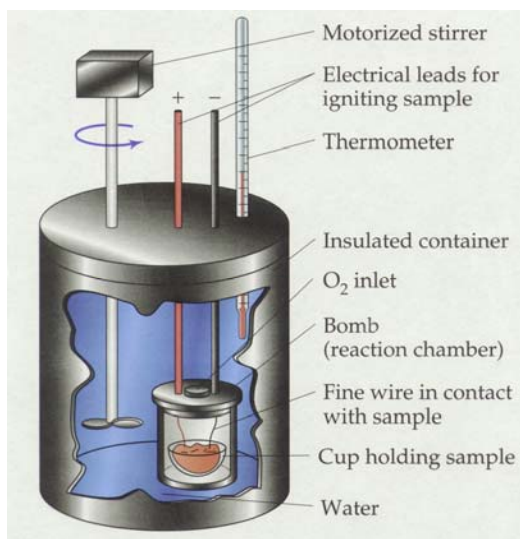
$$T_f = \frac{-324380}{-4850}$$

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

### Energy involved in Chemical Change (Chemical Reaction):

**Molar Heat of Combustion ( $\Delta H_{\text{comb}}$ ):** - the amount of heat released when one mole of reactant is burned with excess oxygen.

- the reaction is often exothermic and therefore  $\Delta H_{\text{comb}} < 0$ .



**Schematic of a Bomb Calorimeter**

### Enthalpy of Combustion

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

$\Delta H$  = Change in Enthalpy       $n$  = moles

$\Delta H_{\text{comb}}$  = Molar Heat of Combustion (kJ/mol)

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

**Chemical Combustion Calorimetry**

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

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

or

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

**Example 7:** Octane,  $\text{C}_8\text{H}_{18(l)}$  was burned completely to  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  in a bomb calorimeter. The following are the observations of the experiment.

Mass of $\text{C}_8\text{H}_{18(l)}$ burned	32.65 g
Initial Temperature of Calorimeter and Water	16.50°C
Final Temperature of Calorimeter and Water	77.30°C
Heat Capacity of Calorimeter	24.70 kJ/°C

- Determine the experimental molar heat of combustion of  $\text{C}_8\text{H}_{18(l)}$ .
- The theoretical  $\Delta H_{\text{comb}}$  for  $\text{C}_8\text{H}_{18(g)}$  is  $-5470.1$  kJ/mol, calculate the % error of this experiment.

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

$$n_{\text{octane}} = \frac{32.65 \text{ g}}{114.26 \text{ g/mol}} = 0.2857517942 \text{ mol } \text{C}_8\text{H}_{18}$$

$$C_{\text{cal}} = 24.70 \text{ kJ/}^\circ\text{C}$$

$$\Delta T = T_f - T_i = 77.30^\circ\text{C} - 16.50^\circ\text{C}$$

$$\Delta T = 60.80^\circ\text{C}$$

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

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

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

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

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

(negative sign is added because  $\Delta H_{\text{comb}}$  is exothermic)

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

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

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

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

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

**Enthalpy of Chemical Reactions**

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

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

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

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

$\Delta H$  = Change in Enthalpy

$n$  = moles

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

$\Delta H_{\text{neut}}$  = Molar Heat of Neutralization (kJ/mol)

$\Delta H_{\text{ion}}$  = Molar Heat of Ionization (kJ/mol)

$\Delta H_{\text{comb}}$  = Molar Heat of Combustion (kJ/mol)

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

A Simple Styrofoam Calorimeter



### Non-Combustion Calorimetry

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

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

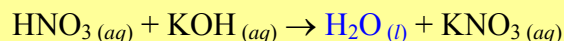
$$n_{\text{sample}}\Delta H_{\text{fus}} = m_w c_w \Delta T \quad (\text{physical change - molar heat of fusion})$$

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

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

**Example 8:** When 250.0 mL of  $\text{HNO}_3(aq)$  at 0.300 mol/L is reacted with 250.0 mL of  $\text{KOH}(aq)$  at 0.300 mol/L, the temperature of the final mixture reached  $28.60^\circ\text{C}$  from  $22.10^\circ\text{C}$ . Determine the molar heat of neutralization between  $\text{HNO}_3(aq)$  and  $\text{KOH}(aq)$ .

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



Assuming  $\text{KNO}_3(aq)$  does not affect the specific heat of water, we would have **500.0 mL of water produced**. Since we have **equal moles of acid and base** ( $0.300 \text{ mol/L} \times 0.2500 \text{ L} = 0.0750 \text{ mol}$ ), the  $\Delta H_{\text{neut}}$  for  $\text{HNO}_3$  would be the same as  $\text{KOH}$ .

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

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

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

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

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

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

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

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

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

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

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

### Assignment

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

6.5 pg. 256 #29 to 38

**6.6: Standard Enthalpies of Formation and Reaction**

**Standard State:** - standard conditions of 1 atm and 25°C. It is denoted by a superscript “°”.

**Standard Molar Enthalpy of Formation ( $\Delta H_f^\circ$ ):** - the amount of heat required / given off to make 1 mole of compound from its elemental components under standard conditions.

- the **Molar Heat of Formation of ALL ELEMENTS is 0 kJ.**
- the **state of the compound affects the magnitude of  $H_f$ .**  
( $H_2O_{(g)}$  has  $\Delta H_f^\circ = -241.8$  kJ/mol;  $H_2O_{(l)}$  has  $\Delta H_f^\circ = -285.8$  kJ/mol)

(See Appendix 3 on pg. A8 to A12 in the Chang 9<sup>th</sup> ed. Chemistry textbook for a list of  $\Delta H_f^\circ$ )

**Standard Enthalpy of Formation (Chemical)**

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

$\Delta H$  = Change in Enthalpy     $n$  = moles     $\Delta H_f^\circ$  = Standard Molar Enthalpy of Formation (kJ/mol)

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

$$\begin{aligned} \Delta H &= -822 \text{ kJ} \\ n &= 2 \text{ mol of NaCl} \\ \Delta H_f^\circ &= ? \end{aligned}$$

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

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

**Example 2:** What is the amount of heat absorbed / released when 100. g of  $\text{CO}_{2(g)}$  is produced from its elements ( $\text{CO}_2$  has  $\Delta H_f^\circ = -393.5$  kJ/mol)?

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

$$\begin{aligned} \Delta H &= n\Delta H_f^\circ \\ \Delta H &= (2.272210861 \text{ mol})(-393.5 \text{ kJ/mol}) \end{aligned}$$

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

$$\Delta H = ?$$

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

**Example 3:** Iron (III) oxide, rust, is produced from its elements, iron and oxygen. What is the mass of rust produced when 1.20 MJ is released when iron is reacted with oxygen ( $\Delta H_f^\circ = -822.2$  kJ/mol for  $\text{Fe}_2\text{O}_3$ )?

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

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

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

$$n = ?$$

$$m = ?$$

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

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

**Example 4:** Calculate the standard molar enthalpy of formation of silver (I) oxide when 91.2 g of  $\text{Ag}_2\text{O}$  is produced from its elements and 12.2 kJ of heat is released from the process.

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

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

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

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

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

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

**Standard Molar Enthalpy of Reaction ( $\Delta H^\circ_{\text{rxn}}$ ):** - the amount of heat involved when 1 mol of a particular product is produced or 1 mol of a particular reactant is consumed under standard conditions of 1 atm and 25°C.

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

- it is equal to **the difference between of all enthalpies of products and all enthalpies of reactants.**
- if the reaction is a **combustion**, it is called the **molar heat of combustion.**

**Direct Method to determine Standard Enthalpy of Reaction**

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

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

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

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

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

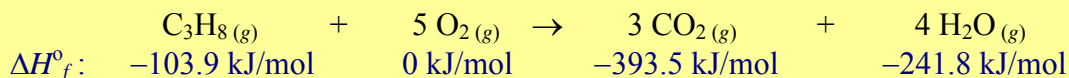
a. Calculate the standard molar enthalpy of combustion for propane.

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

b. Draw its potential energy diagram.

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

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



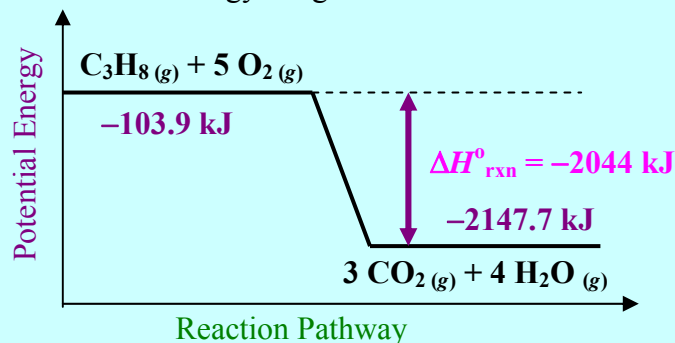
$$\Delta H^\circ_{\text{rxn}} = \Sigma H^\circ_{\text{products}} - \Sigma H^\circ_{\text{reactants}}$$

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

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

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

b. Potential Energy Diagram



c. From part a., for every 1 mol of  $\text{C}_3\text{H}_8$  burned, 2043.8 kJ is released.

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

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

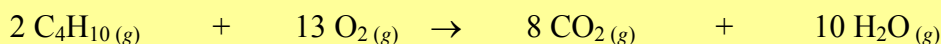
$$\Delta H = n\Delta H^\circ_{\text{rxn}}$$

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

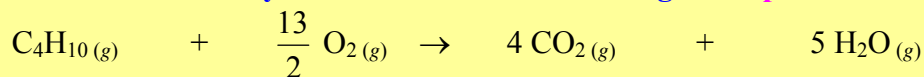
$$\Delta H = -695 \text{ kJ} \quad (695 \text{ kJ is released})$$

**Example 6:** Find the amount of heat released when 34.9 g of butane gas is burned at standard conditions.  
 $(\Delta H_f^\circ \text{C}_4\text{H}_{10} = -124.7 \text{ kJ/mol}; \Delta H_f^\circ \text{CO}_2 = -393.5 \text{ kJ/mol}; \Delta H_f^\circ \text{H}_2\text{O}_{(g)} = -241.8 \text{ kJ/mol})$

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



(We have to divide all coefficients by 2 because we are calculating  $\Delta H_{\text{rxn}}$  per mol of butane burned.)



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

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

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

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

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

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

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

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

$$\Delta H = ?$$

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

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

a. determine the experimental standard molar enthalpy of combustion heptane.

b. find the theoretical standard molar enthalpy of combustion of heptane.

$$(\Delta H_f^\circ \text{ heptane} = -224.2 \text{ kJ/mol})$$

c. explain why the experimental  $\Delta H^\circ_{\text{rxn}}$  is different than its theoretical counterpart.

a. We use the conservation of heat to calculate experimental  $\Delta H_{\text{rxn}}$ .

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

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

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

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

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

$$\Delta H^\circ_{\text{rxn}} = ?$$

$$n \Delta H^\circ_{\text{rxn}} = m_w c_w \Delta T$$

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

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

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

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



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

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

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

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

c. Some of the possible reasons why experimental  $\Delta H^\circ_{rxn}$  ( $-4.08$  MJ) is different than the theoretical  $\Delta H^\circ_{rxn}$  ( $-4.46$  MJ)

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

**Example 8:** HCOOH (g) were completely burned to CO<sub>2</sub> (g) and H<sub>2</sub>O (l) in a calorimeter. The following are the observation of the experiment.

Mass of HCOOH <sub>(g)</sub> burned	9.22 g
Initial Temperature of Calorimeter and Water	21.5°C
Final Temperature of Calorimeter and Water	37.3°C
Heat Capacity of Calorimeter and Water	3.20 kJ/°C

- a. Determine the experimental molar enthalpy of formation of HCOOH (l) assuming standard conditions. ( $\Delta H^\circ_f$  CO<sub>2</sub> =  $-393.5$  kJ/mol;  $\Delta H^\circ_f$  H<sub>2</sub>O (l) =  $-285.8$  kJ/mol)
- b. If the theoretical  $\Delta H^\circ_f$  for HCOOH (g) is  $-363$  kJ/mol, calculate the % error of this experiment.

a. We use the conservation of heat to calculate experimental  $\Delta H_{rxn}$ .

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

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

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

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

$$\Delta H^\circ_{rxn} = ?$$

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

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

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

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

Next, we use the direct method to find the  $\Delta H^\circ_f$  of HCOOH.



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

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

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

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

$$\text{Experimental } \Delta H^\circ_f \text{ of HCOOH} = -427 \text{ kJ/mol}$$

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

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

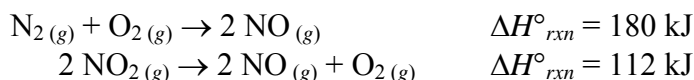
$$\% \text{ error} = 17.6\%$$

**Hess's Law:** - the indirect method of obtaining overall  $\Delta H^\circ_{rxn}$  of a net reaction by the **addition of  $\Delta H^\circ_{rxn}$**  of a series of reactions.

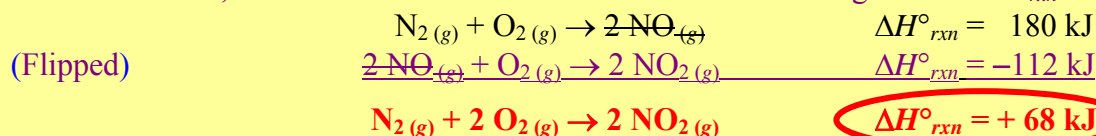
- when adding reactions, **compare the reactants and products of the overall net reaction with the intermediate (step) reactions given. Decide on the intermediate reactions that need to be reversed and / or multiply by a coefficient, such that when added, the intermediate products will cancel out perfectly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

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

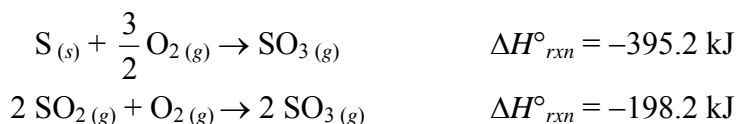
**Example 9:** Calculate  $\Delta H^\circ_{rxn}$  for the reaction  $N_2(g) + 2 O_2(g) \rightarrow 2 NO_2(g)$ , when the following reactions are given.



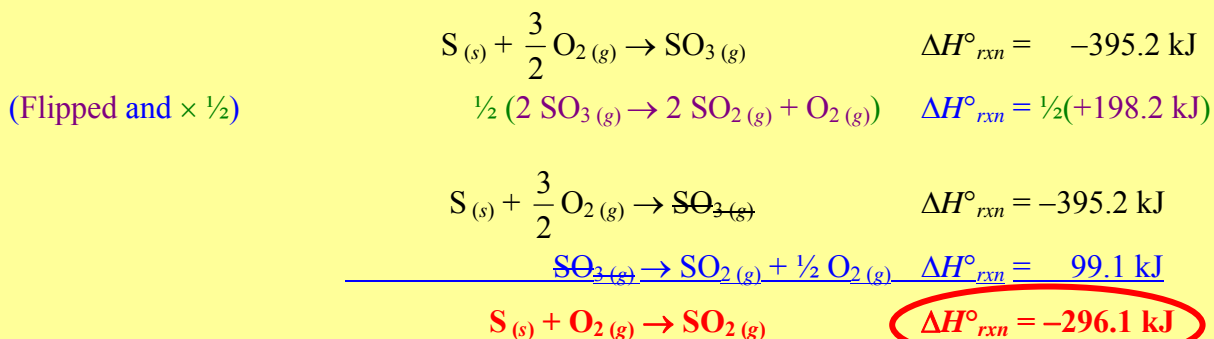
Note that 2  $NO_2$  in the net reaction is on the product side, whereas 2  $NO_2$  in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the  $\Delta H^\circ_{rxn}$ .



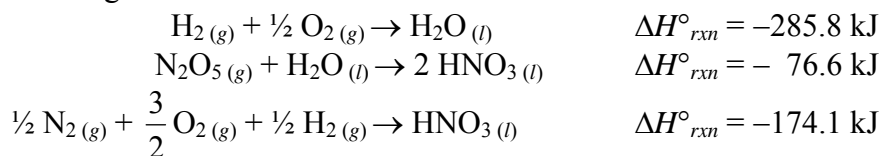
**Example 10:** Determine the  $\Delta H^\circ_{rxn}$  for the reaction  $S(s) + O_2(g) \rightarrow SO_2(g)$ , when the following reactions are given.



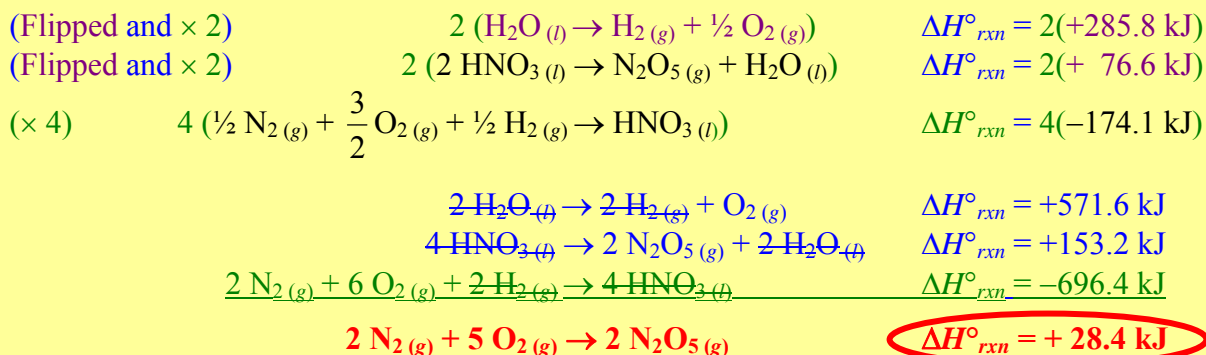
- $SO_2$  in the net reaction is on the product side, whereas 2  $SO_2$  in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the  $\Delta H^\circ_{rxn}$ .
- There is only 1  $SO_2$  in the net reaction, whereas there are 2  $SO_2$  in the second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



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



- $2 \text{N}_2\text{O}_5$  in the net reaction is on the product side, whereas  $\text{N}_2\text{O}_5$  in the second reaction is on the reactant side. Hence, we need to reverse the second reaction and its sign of the  $\Delta H^\circ_{rxn}$ .
- There are  $2 \text{N}_2\text{O}_5$  in the net reaction, whereas there is only  $1 \text{N}_2\text{O}_5$  in the second reaction. Therefore the second reaction and its  $\Delta H^\circ_{rxn}$  need to be multiplied by the coefficient of 2.
- There are  $2 \text{N}_2$  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  $\Delta H^\circ_{rxn}$  by the coefficient of 4.
- In order for  $\text{H}_2\text{O}$  to cancel from the first and second reactions, we have to multiply the first reaction by 2 and flipped. This is because  $\text{H}_2\text{O}$  in the second reaction has also flipped and has been multiplied by 2.



### Assignment

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

### 6.7: Heat of Solution and Dilution

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

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

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

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

### Enthalpy of Solution

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

$$\Delta H_{soln} = U + \Delta H_{hydr} \quad (\text{for ionic solutions})$$

$\Delta H$  = Change in Enthalpy     $n$  = moles

$\Delta H_{soln}$  = Molar Enthalpy of Solution (kJ/mol)

$U$  = Lattice Energy (kJ/mol)

$\Delta H_{hydr}$  = Molar Enthalpy of Hydration (kJ/mol)

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

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

**Example 1:** A cold pack consists of 40.0 g of  $\text{NH}_4\text{NO}_3$  is dissolved in water. How much energy is absorbed or released into its surrounding if the  $\Delta H_{soln}$  is 26.2 kJ/mol?

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

(Heat is absorbed from the surrounding)

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

$$\Delta H = (0.499625281 \text{ mol})(26.2 \text{ kJ/mol})$$

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

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

$\Delta H = ?$

**Example 2:** 12.9 kJ of heat is released when  $\text{CaCl}_2$  is dissolved in water, find the mass of  $\text{CaCl}_2$  dissolved if the molar enthalpy of solution of  $\text{CaCl}_2$  is  $-82.8$  kJ/mol.

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

(Heat is released into the surrounding)

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

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

$$n = ?$$

$$m = ?$$

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

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

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

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

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

(**Examples:** When  $\text{NaOH}_{(s)}$  is dissolved to become  $\text{NaOH}_{(aq)}$ , it releases heat. During the dilution process, the solution gets even warmer. This is because more intermolecular forces form between the added water molecules and the ions present. More intermolecular forces or bonds form mean more heat is released. Similarly, when concentrated  $\text{H}_2\text{SO}_{4(aq)}$  is diluted, more intermolecular forces are made and the process releases a lot of heat. Hence, we always add concentrated to water slowly with constant stirring.)

### Assignment

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**6.8: Present Sources of Energy and New Energy Sources**

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

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

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

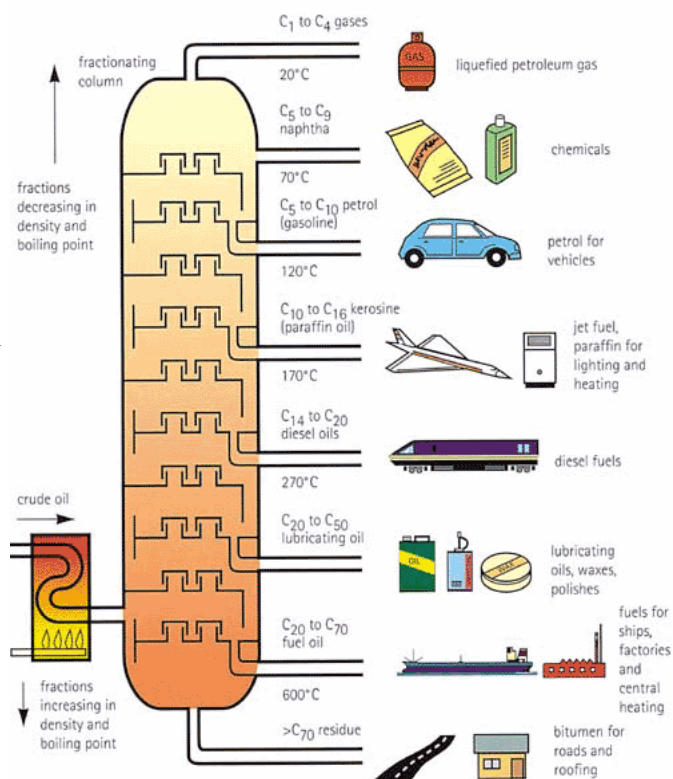
**Example:** Propane burns completely.  $C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g)$

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

**Example:** Incomplete combustion of Propane.  $C_3H_8(g) + 4 O_2(g) \rightarrow 2 CO(g) + CO_2(g) + 4 H_2O(g)$

- 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.

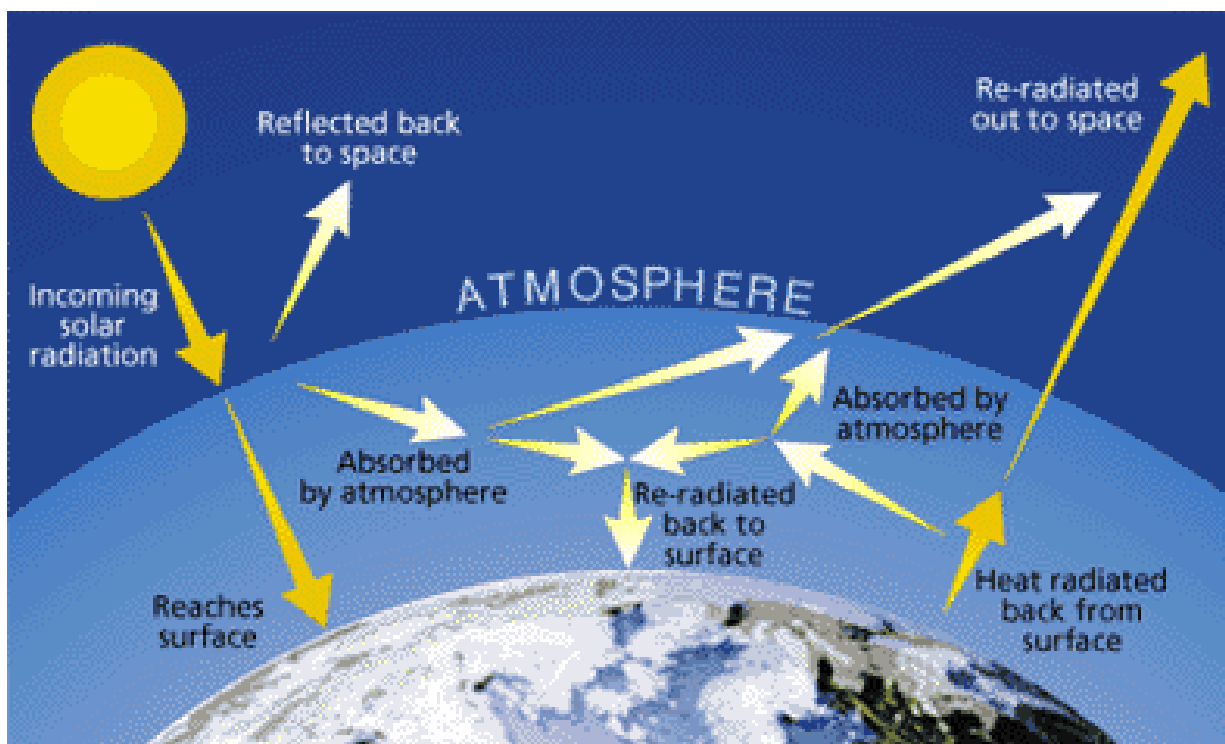
- branched alkanes are easier to burn and has a higher octane value in gasoline. (isooctane or 2,2,4-trimethylpentane has the best octane rating – assigned as 100)

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  $\text{SO}_2$  and  $\text{SO}_3$ , which is the main source of air pollution and acid rain.

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



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

1. **Carbon dioxide (CO<sub>2</sub>)** is released to the atmosphere when solid waste, fossil fuels (oil, natural gas, and coal), and wood and wood products are burned.
2. **Methane (CH<sub>4</sub>)** is emitted during the production and transport of coal, natural gas, and oil. Methane emissions also result from the decomposition of organic wastes in municipal solid waste landfills, and the raising of livestock.
3. **Nitrous oxide (N<sub>2</sub>O)** is emitted during agricultural and industrial activities, as well as during combustion of solid waste and fossil fuels.
4. **Hydrofluorocarbons (HFCs), Perfluorocarbons (PFCs), and Sulfur Hexafluoride (SF<sub>6</sub>)** are very powerful greenhouse gases that are not naturally occurring that are generated in a variety of industrial processes.

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

- Automobiles and Major Transportations account for 34% of CO<sub>2</sub> emissions globally (Power Plants contributes 33%; Major Industries and Home Heating contribute the remaining 33%).
- Presently 89% of Energy Productions involve the burning of Fossil Fuels (Coal, Petroleum, Natural Gas and Biomass).
- Heat and Electricity generated from combustion of fossil fuel is at most 30% efficient.

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

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

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

**Alternate Energy Sources without the Emission of Greenhouse Gas**

- 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 various landscapes.
- Geothermal Power**: - the use of underground steam to generate electricity.
  - very efficient and reliable, but location specific.
  - geothermal power is widely use in Iceland where it is sitting on the Atlantic ridge and there are lots of hot springs.
- Tidal Power**: - the use of tidal current to generate electricity.
  - very efficient and somewhat reliable, but location specific.
  - tidal power involves placing electric turbines at a narrow mouth of a channel where normal tides can cause bigger current and quick rise in water levels. It is being used in the Bay of Fundy at Nova Scotia, Canada and Kvalsund at the Arctic tip of Norway.
  - tidal power can sometimes disrupt migratory routes of marine species.
- 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.