*Chapter 6: Thermochemistry

*6.1: Energy and it's Units:

*energy: the potential or capacity to move matter.

*We will explore the meaning of kinetic, potential, and internal energy:

1] Kinetic Energy: is the energy associated with an object by virtue of its motion "moving".

$$\boxed{KE = \frac{1}{2} m V^2}$$

⇒ the SI unit of energy $Kg \cdot m^2/s^2$ = joule(J)

⇒ Calorie (cal) is a non-SI unit of energy commonly used by chemists, originally defined as the energy required to arise th temperature of one gram of water 1°C.

$$\boxed{1\ cal = 4.184\ J}$$

⇒ watt = joule/s

*Example: A ball can travels between 60 and 90 miles per hr. A regular ball weighing 143 g travels 75 miles per hr (33.5 m/s). what is th KE of this ball in Joules? in calories?

$$E_K = \frac{1}{2} \times m \times V^2 = \frac{1}{2} \times 0.143\ Kg \times (33.5\ m/s)^2$$

$$= \boxed{80.2\ J} \times \frac{1\ cal}{4.184\ J} = \boxed{19.2\ cal}$$

2] Potential Energy: the energy an object has by virtue of its position in a field of force.

$$\boxed{E_p = mgh}$$

⇒ $g = 9.807\ m/s^2$
m = mass
h = height

3] Internal Energy: is the sum of the kinetic energy and potential energy of the particles making up a substance.

$$\boxed{E_{tot} = E_K + E_p + U}$$

⇒ U is the internal energy

* law of Conservation of Energy: ⇒ first law of thermo dynamics.

"Energy may be converted from one form to another, but the total quantity of energy remains constant"

*6.2: First law of Thermodynamics; Work and Heat

* Thermodynamic system: the substance or mixture of substances that we single out ~~of~~ for study (Perhaps including vessel) in which a change occures, and it can be called simply the system.

* Surroundings: everything in the vicinity of the thermodynamics system (it's environment).

* Work and Heat:

work: is an energy transfer (or energy flow) into or out of a thermodynamic system whose effect on the surroundings is equivalent to moving an object through a field of force (w)

Heat (q): is an energy transfer (energy flow) into or out of a thermodynamic system that results from a temperature difference between the system and its surroundings.

Process	Sign
work done by the system on the surroundings →	−
work done on the system by the surroundings →	+
Heat absorbed by the system from the surroundings (endothermic) →	+
Heat absorbed by the surroundings from the system (exothermic) →	−

* Change in internal energy "U" $\boxed{\Delta U = U_f - U_i}$

* Internal energy is an **extensive property**, that is, it depends on the amount of substances in the system

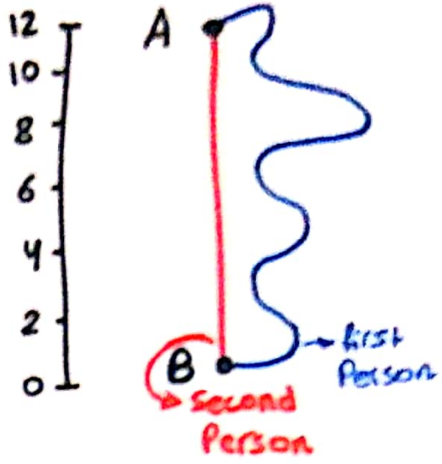
* Internal energy is also a state function.

⇒ state function: is a property of a system that depends only on its present state, which is determined by variables such as temperature and pressure and which is independent of any previous history of the system.

Path function: depend on the way (history)

* first law of thermodynamics: the change in internal energy of a system, ΔU, equals $q+w$ (heat plus work).

$$\boxed{\Delta U = q + w}$$



* Person 1 has the same potential energy as 2nd person.

*** Example:** The work done when a gas is compressed in a cylinder is 462 J. During this process, there is a heat transfer of 128 J from the gas to the surroundings. Calculate the energy change for this process:

$w = +462\,J$

$q = -128\,J$

$$\Delta U = q + w$$
$$= -128 + 462$$
$$= 334\,J$$

*6.3: Heat of Reaction; Enthalpy of Reaction

*exothermic process: a chemical reaction or physical ~~state~~ change in which heat is envolved or is released from the system. (q is negative)

*endothermic process: a chemical reaction or a physical change in which heat is ~~envolved~~ absorbed by the system. (q is positive)

* Pressure-Volume Work:

=> equals the negative of the pressure times the change in volume of the system.

$$\boxed{w = -P\Delta V}$$ in Pa and m^3

$1\ atm.L = 101.3\,J$

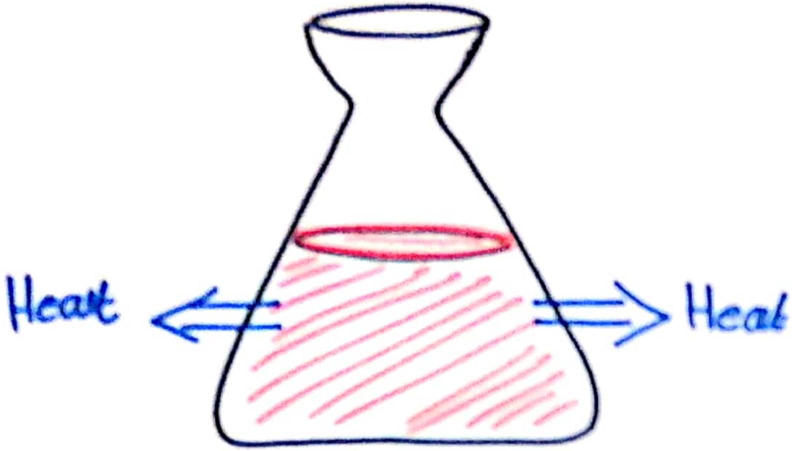
$1\,atm = 1.013 \times 10^5\ Pa$

$1L = 1dm^3 = 10^{-3} m^3$

$= 1.013 \times 10^2$

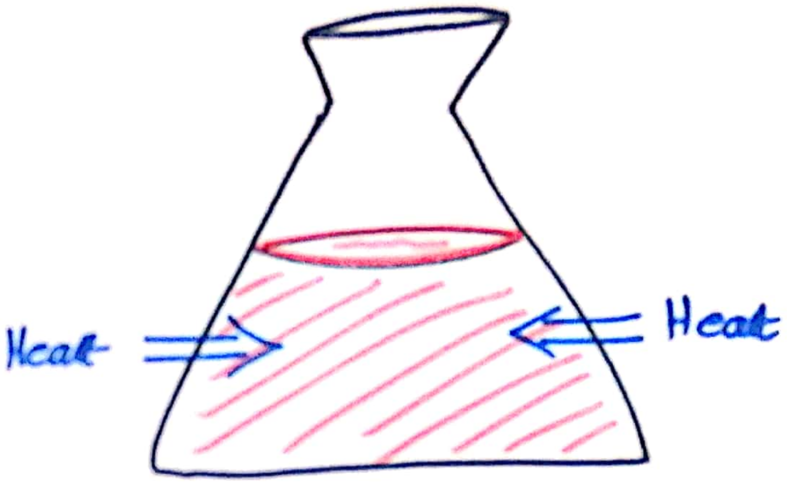
$= 1.01.3$

$q = -$



Exothermic

$q = +$



Endothermic

at95

⇒ ignore volume of H_2O

⇒ 1 atm L = 101.3 J

*** Example:** $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$

the heat of reaction at $\underline{77°C}$ $^{+273 = 350K}$ and $\underline{1\,atm}$ is $-885.5\,kJ$.

- what is the change in volume when $\underline{1.00\,mol}$ of CH_4 reacts with $\underline{2.00\,mol\ O_2}$?
- what is w?
- calculat ΔU for the change indicated by the chemical equation?

ⓐ $\Delta V = V_{final} - V_{initial} = \dfrac{n_f RT}{P} - \dfrac{n_i RT}{P} = \dfrac{\Delta n RT}{P} = \dfrac{(1-3) \times 0.0821 \times 350}{1}$

$= -57.44\,L$

ⓑ $W = -P\Delta V = -1\,atm \times -57.44\,L$

$= 57.44\,atm.L \times 101.3 = 5818\,J$

$= 5.8\,KJ$

ⓒ $\Delta U = q + w = -885.5\,KJ + 5.8\,KJ = \boxed{-879.7\,KJ}$

* Enthalpy and Enthalpy of Reaction

* Enthalpy (H): the internal of the thermodynamics system **U**, plus pressure **P**, time Volume **V**.

$$\boxed{H = U + PV} \qquad \boxed{\Delta H = H_f - H_i}$$

* H is a state function.

$$\Rightarrow \quad \Delta U = q + W = q - P\Delta V = \underline{q - RT\Delta n} \rightarrow \Delta n = n_{Product} - n_{reactant}$$

$$\Rightarrow \quad q = \Delta U + P\Delta V = (U_f - U_i) + P(V_f - V_i)$$

$$= U_f - U_i + PV_f - PV_i = (U_f + PV_f) - (U_i + PV_i)$$

$$= H_f - H_i$$

$$\boxed{q = \Delta H}$$

at fixed pressure and a given temperature

⇒ we relate to the change in enthalpy, ΔH, for a reaction at a given T and fixed P as **enthalpy of reaction** $\Delta H = H_{Product} - H_{reactants}$

*** Example:** calculate the change in internal energy when 2moles of CO are converted to 2moles of CO_2 at 1atm, and 25°C

$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)} \qquad \Delta H = -566.0\ KJ/mol$$

$q = \Delta H$

$P = 1atm$

$T = 298\ K$

$\Delta n = 2 - 3 = -1$

$$\Delta U = q + W$$

$$= \Delta H - P\Delta V$$

$$= \Delta H - \Delta nRT$$

$$= -566\ \frac{KJ}{mol} - (-1) \times 8.314\ J/\cancel{K}\cdot\cancel{mol} \times 298\cancel{K}$$

$$= -566\ KJ/mol + 2.5\ KJ/mol$$

$$\boxed{= -563.5\ KJ/mol}$$

*6.4: Thermochemical Equations.

* thermochemical equation: chemical equation for a reaction (including phase labels) in which the equation is given a molar interpretation, and the enthalpy of reaction for these molar amounts is written directly after the equation.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)} \; ; \; \Delta H = -368.6\,kJ$$

* two important rules:

1] when a thermochemical equation is multiplied by any factor, the value of ΔH for the new equation is obtained by multiplying the value of ΔH in the original equation by that same factor.

2] when a chemical equation is reversed, the value of ΔH is reversed in sign.

*** Example:** when 2 mol $H_{2(g)}$ and 1 mol $O_{2(g)}$ react to give liquid water, 572 KJ of heat envolves:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \; ; \; \Delta H = -572 \text{ kJ}$$

write the equation for 1 mol of liquid water. ⓐ Give the ⓑ reverse equation, in which 1 mol of liquid water dissociates into hydrogen and oxygen:

ⓐ $H_{2(g)} + 1/2\,O_{2(g)} \longrightarrow H_2O_{(l)} \; ; \; \Delta H = -286 \text{ kJ}$

ⓑ $H_2O_{(l)} \longrightarrow H_{2(g)} + 1/2\,O_{2(g)} \; ; \; \Delta H = 286 \text{ kJ}$

* 6.5: Applying Stoichiometry to Heats of Reaction

$$\text{Mass of A} \xrightarrow[\text{MW A}]{\text{using}} \text{mol A} \xrightarrow[\text{enthalpy of reaction}]{\text{using}} \text{Heat (kJ of heat)}$$

(g of reactants or products)

*** Example:** How much heat is evolved when 9.07×10^5 g of ammonia is produced according to the following equation?

$$N_{2(g)} + 3H_{2(g)} \longrightarrow \textcircled{2}NH_{3(g)} \quad ; \Delta H = -91.8\ kJ \qquad m.W_{NH_3} = 17$$

$$\frac{9.07\times10^5\ \cancel{g}}{17\ \cancel{g}/mol} = \underline{\overset{\times10^5}{0.53}\ \cancel{mol}} \times \frac{-91.8\ kJ}{2\ \cancel{mol}} = \boxed{-24.5\times10^5\ kJ}$$

***Example:** Given the thermochemical equation

$$2SO_{2(g)} + O_{2(g)} \longrightarrow 2SO_{3(g)} \text{ , } \Delta H = -198.2 \text{ kJ/mol}$$

calculate the heat evolved when 87.9 g of SO_2 (M.W =64.07 g/mol) is converted to SO_3?

$$\Delta H = \frac{87.9\,\cancel{g}}{64.07\,\cancel{g}/\text{mol}} \times \frac{-198.2 \text{ KJ}}{2 \text{ mol}} = -135.958 \text{ kJ} \approx \boxed{-136 \text{ KJ}}$$

*Measuring Heats of Reaction (6.6)

* Heat capacity and Specific heat:

Heat Capacity (C): the quantity of heat ~~added~~ needed to raise the temperature of the sample of substance one degree Celsius (or one Kilven).

$$\boxed{q = C\,\Delta t} \Rightarrow$$

Δt is the change in temperature.

Specific Heat Capacity (specific heat): the quantity of heat required to raise the temperature of one gram of a substance by one degree Celsius (ore one Kilven) <u>at constant pressure</u>.

$$\boxed{q = s \times m \times \Delta t}$$

specific heat. mass. the change in temperature.

*** Example:** Calculate the heat absorbed by 15.0 g of water raise its temperatu from 20.0°C to 50.0°C (at constant pressure). The specific heat of water is 4.18 J/(g.°C).

$\Delta t = 50 - 20 = 30°c$

$q = s m \Delta t$

$= 4.18 \times 15 \times 30 = \boxed{1.88 \times 10^3 \ J}$

*Measurement of Heat of Reaction:

→ Calorimeter: a device used to measure the heat absorbed or evolved during a physical or chemical change.

→ Calorimeter also is considered as isolated systems $\boxed{q_{sys} = 0}$

$q_{sys} = 0$

$q_{sys} = q_{water} + q_{cal} + q_{rxn} = 0$

$q_{rxn} = -(q_{water} + q_{cal})$

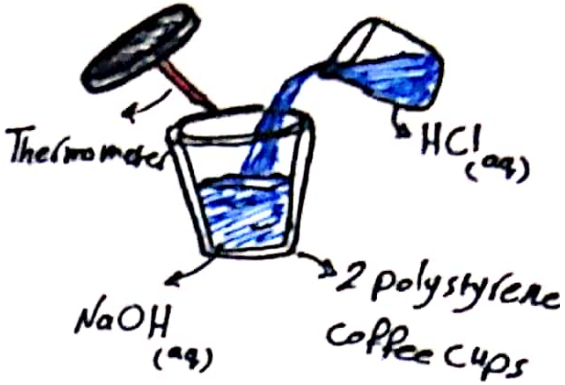
→ from the previous laws:

$q_{water} = m_{*} s_{*} \Delta t$

$q_{cal} = C_{cal} \times \Delta t$

The Coffee-cup Calorimeter: (constant pressure calorimeter):

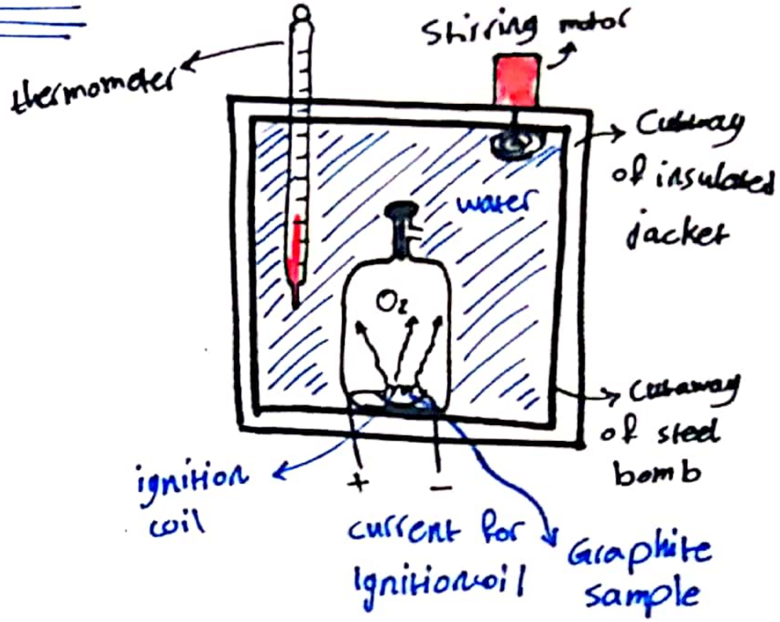
$$q_{rxn} = \Delta H \quad \Rightarrow \quad q_{rxn} = -q_{sol}$$



※ The Bomb Calorimeter: (constant Volume calorimeter):

$q_{rxn} \approx \Delta H$ when the moles of gas remain constant.

$$q_{rxn} = -q_{cal}$$



C

Suppose 0.562 g of graphite is placed in a bomb calorimeter with an excess of oxygen at 25.00°C and 1 atm pressure (Figure 6.16). Excess O_2 ensures that all carbon burns to form CO_2. The graphite is ignited, and it burns according to the equation

$$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta H$$

On reaction, the calorimeter temperature rises from 25.00°C to 25.89°C. The heat capacity of the calorimeter and its contents was determined in a separate experiment to be 20.7 kJ/°C. What is the heat of reaction at 25.00°C and 1 atm pressure? Express the answer as a thermochemical equation. (Note that moles of gas remain constant, so the pressure is constant and the heat of reaction is essentially the enthalpy of reaction.)

$C = 20.7\ \text{kJ}/°\text{C}\ ,\ \Delta t = 0.89°\text{C}\ ,\ m_C = 0.562\text{g}$

$$q_{rxn} = -q_{cal} = -(C_{cal}\ \Delta t) = -20.7\frac{\text{kJ}}{\cancel{°\text{C}}} \times 0.89\cancel{°\text{C}} = \boxed{-18.4\ \text{kJ}}$$

$$n_C = \frac{0.562\cancel{\text{g}}}{12\cancel{\text{g}}}\cdot\text{mol} = 0.0468\ \text{mol}\ \ C$$

$$\Delta H = \frac{q}{0.0468} = -393\ \text{KJ}$$

$$C_{(\text{graphite})} + O_{2(g)} \longrightarrow CO_{2(g)}\ ;\ \Delta H = -393\ \text{kJ}$$

Suppose 33 mL of 1.20 M HCl is added to 42 mL of a solution containing excess sodium hydroxide, NaOH, in a coffee-cup calorimeter. The solution temperature, originally 25.08C, rises to 31.88C. Give the enthalpy change, ΔH, for the reaction:

$$\mathbf{HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H2O_{(l)}}$$

Express the answer as a thermochemical equation. For simplicity, assume that the heat capacity and the density of the final solution in the cup are those of water. (In more accurate work, these values must be determined.) Also assume that the total volume of the solution equals the sum of the volumes of $\mathbf{HCl_{(aq)}}$ and $\mathbf{NaOH_{(aq)}}$.

S

C

$V_{HCl} = 33\,ml$, $M_{HCl} = 1.2$, $V_{NaOH} = 42\,mL$, $V_{sol} = 75\,mL$, $\Delta t = 6.8\,°C$, $C_{H_2O} = 75.3\,J/mol.C$

$m_{sol} = 75\,g$

$S_{H_2O} = 4.18\,J/g.C$

$q_{rxn} = -q_{sol} =$ ~~$-C\Delta t = -75.3\,J/mol.C \times 6.8\,C = 512.04\,\frac{J}{mol}$~~

$= -sm\Delta t = -4.18\,\frac{J}{g.C} \times 75\,g \times 6.8\,C \boxed{= 2131.8\,J}$

$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$, $\Delta H = -53.8\,KJ/m$

$M = \frac{n}{V}$

$1.2 = \frac{n}{33 \times 10^{-3}} \Rightarrow n = 0.0396\,mol\ HCl$

$\Delta H = \frac{-2131.8}{0.0396} = 53833.3\,J/mol$

$= 53.8\,KJ/mol$

*** Example:** when 15.3g of $NaNO_3$ was dissolved in water in a constant-pressure calorimeter, the temperature fell from 25.00°C to 21.56°C. If the heat capacity of the solution and the calorimeter is 1071 J°/C, what is the enthalpy change when 1 mol. of $NaNO_3$ dissolves in water? The solution process is

$$NaNO_{3(s)} \longrightarrow Na^{+}_{(aq)} + NO^{-}_{3(aq)} \; ; \Delta H = ?$$

$m_{NaNO_3} = 15.3g$

$\Delta t = -3.44\,°C$

$C = 1071\ J°/C$

$n = 1mol\ NaNO_3$

$$q_{rxn} = -q_{cal}$$

$$= -1071\,\frac{J}{\cancel{°C}} \times -3.44\,\cancel{°C} = \boxed{3684.2J} \rightarrow \frac{15.3\cancel{g}}{85\cancel{g}}\,mol = 0.18mol$$

$$\Delta H?? \longrightarrow 1mol$$

$$\Delta H = \frac{3684.2}{0.18} = 20467.78\ J/mol$$

$$\boxed{\Delta H = 20.47\ kJ/mol}$$

*6.7: Hess's Law:

"for a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation equals the sum of the enthalpy changes for the individual steps."

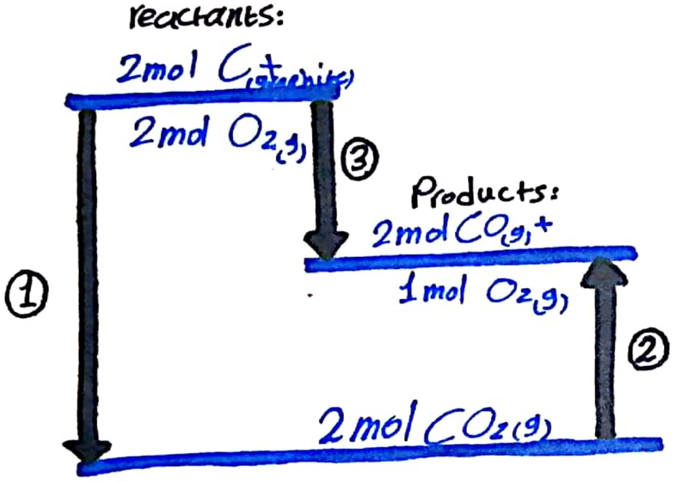
$$2C_{(graphite)} + O_{2(g)} \longrightarrow 2CO_{(g)}$$

1] $2\,C_{(graphite)} + \cancel{2}O_{2(g)} \longrightarrow \cancel{2CO_{2(g)}}$ $\Delta H_1 = (-393.5\text{ kJ}) \times (2)$

+

2] $\cancel{2CO_{2(g)}} \longrightarrow 2CO_{(g)} + \cancel{O_{2(g)}}$ $\Delta H_2 = (-566\text{ kJ}) \times (-1)$

$2\,C_{(graphite)} + O_{2(g)} \longrightarrow 2CO_{(g)}$ $\Delta H_3 = -221.0\text{ kJ}$



***Example:** what is enthalpy of reaction, ΔH, for the formation of tungsten carbide, WC, from the elements?

$$W_{(s)} + C_{(garphite)} \longrightarrow WC_{(s)}$$

1] $\frac{\cancel{2}W_{(s)}}{\cancel{2}} + \frac{3\cancel{O_2}_{(g)}}{2} \longrightarrow \frac{\cancel{2WO_3}_{(s)}}{\cancel{2}}$; $\Delta H = \frac{-1685.8\ kJ}{2}$

2] $C_{(graphite)} + \cancel{\frac{2O_2}{2}}_{(g)} \longrightarrow \cancel{CO_2}_{(g)}$; $\Delta H = -393.5\ KJ$

$\left(3]\ \frac{\cancel{2}WC_{(s)}}{\cancel{2}} + \frac{5O_{2(g)}}{2} \longrightarrow \frac{\cancel{2}WO_{3(s)}}{\cancel{2}} + \frac{\cancel{2CO_2}_{(g)}}{\cancel{2}}\ ;\ \Delta H = \frac{-2391.8 kJ}{2}\right) \times -1$

$\cancel{WO_3} + \cancel{CO_2} \longrightarrow WC + \cancel{5/2\,O_2}$; $\Delta H = \frac{+2391.8}{2}\ KJ$

$W_{(s)} + C_{(graphite)} \longrightarrow WC_{(s)}$; $\Delta H = -40.5$

*6.8: Standard Enthalpies of Formation

* Standard state: the standard thermodynamic conditions chosen for substances when listing or comparing thermodynamic data: 1 atm pressure and the specified temperature (usually 25°C).

* ΔH° is called as the standard enthalpy of reaction.

* allotrope: one of two or more distinct forms of an element in the same physical state.

* reference form: the stablest form (physical state and allotrope) of the element under standard thermodynamic conditions

* The standard enthalpy of formation also called as standard heat of formation: the enthalpy change for the formation of one mole of the substance in its standard state from its elements in their reference form and in their standard states. → (ΔH°_f)

$\underset{\sim}{}CH_{4(g)} + \underset{\sim}{4}Cl_{2(g)} \longrightarrow \underset{\sim}{}CCl_{4(l)} + \underset{\sim}{4}HCl_{(g)}$; $\Delta H^\circ = ??$

$\Delta H_f^\circ\ CH_{4(g)} = -74.87$

$\Delta H_f^\circ\ Cl_{2(g)} = 0$

$\Delta H_f^\circ\ CCl_{4(l)} = -135.4$

$\Delta H_f^\circ\ HCl = -92.31$

$C_{(graphite)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$; $\Delta H_f^\circ = -74.9\ kJ$ x −1

$\cancel{C_{(graphite)}} + 2Cl_{2(g)} \longrightarrow CCl_{4(l)}$; $\Delta H_f^\circ = -135.4\ KJ$

$4\times\cancel{\tfrac{1}{2}H_{2(g)}} + 4\times\tfrac{1}{2}Cl_{2(g)} \longrightarrow 4\times HCl_{(g)}$; $\Delta H_f^\circ = -92.3\ kJ \times 4$

$CH_{4(g)} \longrightarrow \cancel{C_{(graphite)}} + \cancel{2H_{2(g)}}$; $74.9 = \Delta H$

$CH_{4(g)} + 4Cl_{2(g)} \longrightarrow CCl_{4(l)} + 4HCl_{(g)}$; $\boxed{\Delta H_f^\circ = -429.7\ KJ}$

$$\boxed{\Delta H^\circ = \sum \underset{\sim}{n}\,\Delta H_f^\circ\ (\text{Products}) - \sum \underset{\sim}{m}\,\Delta H_f^\circ\ (\text{reactants})}$$

$= 1\times -135.4 + 4\times -92.31 - (1\times -74.87 + 4\times 0)$

$= -429.7\ KJ$

***Example:** use values of ΔH_f° to calculate the heat of vaporization, ΔH_{vap}°, of carbon disulfide at 25°C. The vaporization process is

$$CS_{2(l)} \longrightarrow CS_{2(g)}$$

$$\Delta H_f^\circ = 89.70 \qquad \Delta H_f^\circ = 116.9$$

$$\Delta H_{vap}^\circ = \sum n \Delta H_f^\circ(\text{products}) - \sum m \Delta H_f^\circ(\text{reactants})$$

$$\Delta H_{vap}^\circ = 1 \times 116.9 - 1 \times 89.70$$

$$= 27.2\ \text{KJ}$$

***Example:** Large quantities of ammonia are used to prepare nitric acid. The first step consists of the catalytic oxidation of ammonia to nitric oxide, NO.

$$4NH_{3(g)} + 5O_{2(g)} \longrightarrow 4NO_{(g)} + 6H_2O_{(g)}$$

what is the standard enthalpy change for this reaction?

$\Delta H_f^\circ\ NH_{3(g)} = -45.9$ $\Delta H_f^\circ\ O_{2(g)} = 0$ $\Delta H_f^\circ\ NO_{(g)} = 90.29$ $\Delta H_f^\circ\ H_2O_{(g)} = -241.8$

$$\Delta H^\circ_{rxn} = \sum n\,\Delta H_f^\circ (\text{Prod}) - \sum \Delta H_f^\circ (\text{react}) .m$$

$$= (4\times 90.29 + 6\times -241.8) - (4\times -45.9 + 5\times 0)$$

$$\boxed{\Delta H^\circ_{rxn} = -906\,kJ}$$

***Example:** Given the following data, what is the value of $\Delta H^\circ_f(C_2H_3O_2^-{}_{(aq)})$

$$Na^+_{(aq)} + C_2H_3O^-_{(aq)} + 3H_2O_{(L)} \longrightarrow NaC_2H_3O_2 . 3H_2O_{(s)}$$

note that: $\Delta H_{rxn} = -19.7$ KJ/mol , $\Delta H^\circ_f\ Na^+_{(aq)} = -239.7$, $\Delta H^\circ_f\ NaC_2H_3O_2 . 3H_2O_{(s)} = 710.4$, $\Delta H^\circ_f\ H_2O_{(L)} = 285.9$

$$-19.7 = 1 \times 710.4 - (1 \times -239.7 + 1 \times \Delta H_f + 3 \times 285.9)$$

$$-19.7 - 710.4 = -239.7 + 3 \times 285.9 = -\Delta H^\circ_f\ C_2H_3O^-_{2(aq)} = -112.1$$

$$\boxed{\Delta H^\circ_f\ C_2H_3O_2^-{}_{(aq)} = 112.1 \text{ KJ}}$$