BASICS

In this chapter, we will study the heat changes that take place when a chemical process occurs. Heat (a form of energy) is either evolved or absorbed in the course of chemical reaction. The study of energetics considers the relationship between thermodynamical functions : heat (q), work (W) and internal energy (U or E).

1. Definitions :

System :

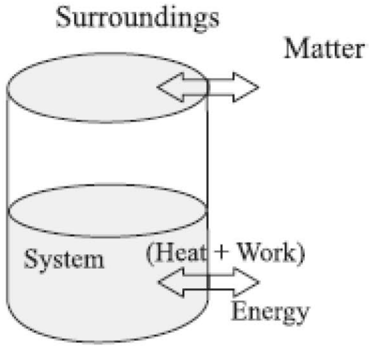
A small portion of the universe with-in which we confine our study of energy changes is called as a *system*.

Surroundings :

The remainder of the universe (i.e., apart from the system), which can interact with the system is called as *surroundings*.

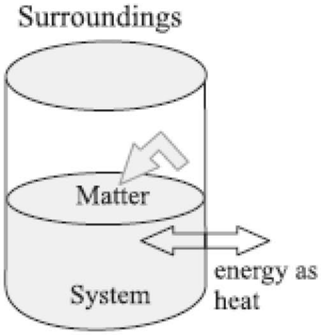
Open System :

This type of system can exchange matter as well as energy with surroundings. The boundary is not sealed and not insulated. Sodium reacting with water in an open beaker is an example of open system.

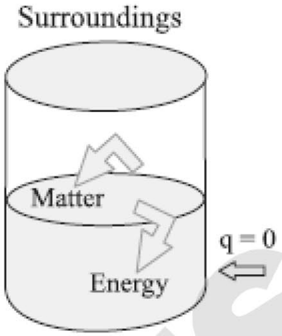


Closed System :

This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed forms a closed system. Heat can be transferred through the walls of the tube to the surroundings but total amount of matter remains the same as vapours cannot escape.



Isolated System :



This type of system has no interaction with its surroundings. Neither matter nor energy can be exchanged with surroundings. A substance contained in an ideal thermos-flask is an example of an isolated system.

2. Thermodynamics Properties :

(i) Intensive Properties :

The properties which do not depend upon the quantity of matter present in the system are called *Intensive properties*. Pressure, temperature, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole (molar volume), concentration, colour potential electrical field electrical resistivity, specific energy, etc. are examples of intensive properties of the system.

(ii) Extensive Properties :

The properties whose magnitude depends upon the quantity of matter present in the system are called *Extensive Properties*. Internal energy, total moles, volume, enthalpy, entropy, Gibbs energy, length, mass, electrical resistance etc. are examples of extensive properties.

3. Internal Energy (U) :

All the possible forms of energy that are associated with a system are referred to as *Internal Energy*. It includes kinetic energy due to all kind of motion of the particles of the system, and their potential energy due to intermolecular forces (interaction). It is impossible to measure the exact value of the internal energy of a system. It can be measured when the system changes its state i.e. as change in internal energy (ΔU).

The internal energy change of a system depends upon the state of the system and not on how the system achieved the particular state. Such a thermodynamic function is called as *state function*. Other examples are: temperature, pressure volume, enthalpy, entropy, Gibbs energy etc.

If U_1 is the internal energy of a system in state 1, and U_2 in the state 2, then the change in the internal energy of the system (ΔU) is given by : $\Delta U = U_2 - U_1$

As stated above, ΔU is independent of the process which takes the system from state 1 to state 2.

4. First law of Thermodynamics :

Energy can neither be created nor destroyed, although it can be transformed from one form to another.

If we supply an amount of heat (= q) to the system in state 1, the system does a work w and goes to achieve the state 2. The heat supplied to the system gets converted into two parts :

(a) Work done by the system

(b) Change in internal energy of the system.

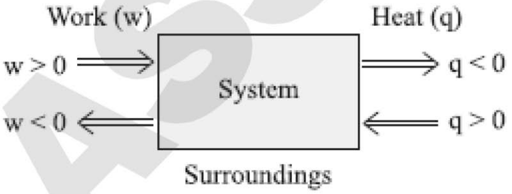
From law of conservation of Energy, we have :

$$q = \Delta U + (-w) \qquad \ldots.(i)$$

This equation is known as *First Law of Thermodynamics*.

5. Sign Convention :

- w is positive, when the work is done on the system.
- w is negative, when the work is done by the system.
- q is positive, when the heat is supplied to the system.
- q is negative, when the heat is lost by the system.



6. Enthalpy :

It is a thermodynamic function (H) defined to study heat changes in chemical reactions. It is also known as heat content of the stem defined as :

$H = U + PV$ where P : Pressure V : Volume

If the change of state takes place at constant pressure, q is denoted as q_p (heat transfer at constant pressure). It is also known as *change in enthalpy* of the system, represented as

$\Delta H = q_p$ (H : Enthalpy of the system).

In such a process, volume of the system will change and work done is given as :

$w = -P\Delta V$ ΔV : change in volume

$\Rightarrow q_p = \Delta U + P\Delta V$ [Using first law of thermodynamics]

or $q_p = U_2 - U_1 + P(V_2 - V_1)$

or $q_p = (U_2 + PV_2) - (U_1 + PV_1)$

or $q_p = H_2 - H_1 = \Delta H$ where $H_1 = U_1 + PV_1$ = enthalpy of the system in state 1

and $H_2 = U_2 + PV_2$ = enthalpy of the system in state 2

Enthalpy change like internal energy change in a *state function*.

Heat change in all chemical reactions is studied as enthalpy change of the reaction ($\Delta_r H$). System in state 1 is taken as *system of reactants and* in state 2 taken *as system of products*. Enthalpy change (Heat change) accompanying the reaction is given as :

$$\Delta_r H = \text{Enthalpy of products} - \text{Enthalpy of reactants} = \sum (H_{\text{product}}) - \sum (H_{\text{reactants}})$$

If the change of state takes place at constant volume, q is denoted as q_v (heat transfer at constant volume).

$$\Delta U = q_v$$

7. Exothermic and Endothermic reactions :

(a) Exothermic reactions :

Chemical reactions in which heat is evolved are known as exothermic reactions.

For example :

$$2Mg(s) + O_2(g) \longrightarrow 2MgO(g)$$

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

Both of the above reactions are exothermic reactions because heat is evolved in them.

In general, an exothermic reaction is represented as : Reactants $\longrightarrow$ Products + heat

Here enthalpy (or heat content) of reactions is partially transferred to the enthalpy of the products and partially evolved as heat.

If H_R : enthalpy of reactants and H_P : enthalpy of products

Clearly, $H_P < H_R \Rightarrow \Delta_r H < 0 \quad [\Delta_r H = H_P - H_R]$

i.e. for exothermic reaction, $\Delta_r H$ (reaction enthalpy) will bear a – ve sign (evolution of heat)

Note : In exothermic reaction, for some time (i.e. during the change) temperature of the products will rise above room temperature. But, very soon the heat is lost to surroundings and the same temperature is maintained.

(b) Endothermic Reactions :

Chemical reactions in which the heat is absorbed from the surroundings are known as *endothermic reactions*.

For example :

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

Both of the above reactions are endothermic reactions because in them heat is absorbed from the surroundings.

In general, an endothermic reaction can be expressed as :

Reactants + heat $\longrightarrow$ Products

Here, enthalpy of products is derived from enthalpy of reactants plus the absorbed heat.

Clearly $H_P > H_R$

$\Rightarrow$ $\Delta_r H > 0$ $[\Delta_r H = H_P - H_R]$

i.e. for endothermic reactions, $\Delta_r H$ (reaction enthalpy) will bear a +ve sign (absorption of heat)

> **Note :** In endothermic reactions, (unlike exothermic reactions), temperature of the reacting mixture falls during the change. But very soon, heat is absorbed from the surrounding and same temperature is restored.

8. Enthalpy Change at Standard Conditions :

$\Delta_r H$ depends upon the conditions under which a reaction is performed. So to compare enthalpy changes of various reactions, they are performed at standard conditions.

Standard conditions for temperature and pressure are 298 K (or 25°*C*) and 1.0 atm pressure. Any enthalpy change measured under these conditions is known as *Standard Enthalpy change* or *Standard Heat of reaction* and it is denoted as $\Delta_r H^{\Theta}$.

It is also important to specify the states of all reactants and products in a reaction. ['*s*' for solids, '*l*' for liquids, '*g*' for gases (or free atoms), '*aq*' for solution in water].

A chemical reaction which clearly informs about the heat change accompanying it (i.e. exothermic or endothermic) and the physical state of all reactants and products is known as *Thermochemical Equation*.

For example :

$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g) \; ; \qquad \Delta_r H_1 = -385.2 \text{ kJ (Exothermic)}$$

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g) \; ; \qquad \Delta_r H = +90.25 \text{ kJ (Endothermic)}$$

> **Note :** $\Delta_r H$ is the reaction enthalpy for a reaction in any form (i.e. stoichiometric coefficients) e.g. refer to the reaction below :
>
> $$2C(s) + O_2(g) \longrightarrow 2\,CO(g) \; ; \qquad \Delta_r H_2 = -770.4 \text{ kJ (Exothermic)}$$
>
> Here, $\Delta_r H_2 = 2\,\Delta_r H_1$

9. Enthalpy of a Compound :

To define the enthalpy of a compound, it is taken that the enthalpy of an element in its most stable state at standard conditions is zero.

Standard states of some elements :

C : Graphite ; S : Rhombic ; Br as $Br_2(\ell)$; I as $I_2(s)$; H as $H_2(g)$;
Cl as $Cl_2(g)$; N as $N_2(g)$; O as $O_2(g)$;
P : White (Exception : Red Phosphorus is more stable than White Phosphorus)

e.g. $H^{\Theta}_{Cl_2(g)} = 0$; $H^{\Theta}_{H_2(g)} = 0$; $H^{\Theta}_{O_2(g)} = 0$; $H^{\Theta}_{Br_2(\ell)} = 0$; $H^{\Theta}_{I_2(s)} = 0$;

Consider the following thermochemical equations at 25°C and 1 atm.

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$

It represents formation of HCl at standard conditions i.e. $\Delta_f H^{\Theta} = \Delta H$ of given reaction

From definition : $\Delta_r H = \Sigma\,(H_{products}) - \Sigma\,(H_{reactants}) = \Sigma\, a_i\,(H)_{m,\ products} - \Sigma\, b_i\,(H)_{m,\ reactants}$

[H_m is the molar enthalpy of the compound and a_i & b_i the stoichiometric coefficients of products and reactants respectively]

$\Rightarrow$ $\Delta_r H^{\Theta} = \Delta_f H^{\Theta} = H^{\Theta}_{HCl} - \left(\frac{1}{2}H^{\Theta}_{H_2} + \frac{1}{2}H^{\Theta}_{Cl_2}\right)$ [see definition of $\Delta_f H^{\Theta}$ in Section – 2]

$\Rightarrow$ $\Delta_f H^{\Theta} = H^{\Theta}{}_{HCl} - 0$ [Enthalpy of elements in standard state = 0]

$\Rightarrow$ $H^{\Theta}_{(HCl)} = \Delta_f H^{\Theta}_{(HCl)}$

Hence the enthalpy of a compound is the standard heat of formation of the compound OR *enthalpy of a compound is often taken as standard enthalpy of formation of that compound.*

Enthalpy of a compound A at standard conditions = $\Delta_f H^{\Theta}$ of A

Note : By convention, $\Delta_f H^{\Theta}\left(H^+(aq)\right) = 0$

Illustration - 1 *How much heat is evolved by the preparation of* 100 *gm of iron by the following reaction ?*

$2\,Al(s) + Fe_2O_3(s) \longrightarrow 2\,Fe(s) + Al_2O_3(s)$; $\Delta_r H = -202.6$ *kcal/mol*

SOLUTION :

From thermochemical reaction, it is clear that 202.6 kcal of heat is involved when two moles of *Fe* (iron) is formed.

$\Rightarrow$ 2 moles of Fe $\equiv$ 202.6 kcal

$\Rightarrow$ 1 mole of Fe $\equiv$ 101.3 kcal

$\Rightarrow$ 100/56 mole of Fe $\equiv$ 101.3 × 100/56 = 180.9 kcal

Heat of Reaction

The heat of a reaction can be assigned special names in the following manner :

(a) Standard Heat of Formation ($\Delta_f H^\Theta$) :

The heat evolved or absorbed when one mol of any compound is formed from its elements in their standard states. It is usually denoted by $\Delta_f H^\Theta \cdot \Delta_f H^\Theta$ can be given –ve or +ve sign, depending upon whether formation is exothermic or endothermic.

$$C(s,\ graphite) + 2\,H_2(g) \longrightarrow CH_4(g) \quad ; \quad \Delta_f H^\Theta = -\,74.3 \text{ kJ/mol}$$

$$\frac{1}{2} H_2(g) + \frac{1}{2} I_2(s) \longrightarrow HI(g) \quad ; \quad \Delta_f H^\Theta = 25.92 \text{ kJ/mol}$$

Note : To write chemical equations for formation, balance the reaction for one mole of compound whose formation is to be studied.

(b) Standard Heat of Combustion ($\Delta_c H^\Theta$) :

The heat evolved (or enthalpy change) when one mole of any substance is completely burnt in excess of oxygen.

$\Delta_c H^\Theta$ will always bear –ve sign for it being enthalpy change of an exothermic reaction.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(\ell) \quad ; \quad \Delta_c H^\Theta = -212 \text{ kcal/mol}$$

$$C(s,\ graphite) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta_c H^\Theta = -94 \text{ kcal/mol}$$

Note : To write chemical equations for combustion, balance the reaction for one mole of compound whose com bustion is to be studied.

Illustration - 2

Calculate $\Delta_r H^\Theta$ *for the reaction :* $C_6H_6(\ell) + \frac{15}{2} O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(\ell)$

Given the standard heat of formations ($\Delta_f H^\Theta$) *of* $H_2O(\ell)$, $CO_2(g)$ *and* $C_6H_6(\ell)$ *are* – 57.80 *kcal/mol*, – 94.05 *kcal/mol and* 19.8 *kcal/mol respectively*.

SOLUTION :

Whenever, standard heat of formation ($\Delta_f H^\Theta$) *of a compound is given it means that enthalpy of that particular compound at standard state is given*. Also, note that in the question, molar enthalpy changes are given.

Using the definition of enthalpy change as : $\Delta_r H = \Sigma H_{(\text{products})} - \Sigma H_{(\text{reactants})}$

For the given reaction : $\Delta_r H^{\Theta} = \Sigma(H^{\Theta}_{\text{products}}) - \Sigma(H^{\Theta}_{\text{reactants}})$

or $\Delta_r H^{\Theta} = \Sigma(\Delta_f H^{\Theta}_{\text{products}}) - \Sigma(\Delta_f H^{\Theta}_{\text{reactants}})$

$$C_6H_6(\ell) + \frac{15}{2}O_2(g) \longrightarrow 6\,CO_2(g) + 3\,H_2O(\ell)$$

$\Delta_f H^{\Theta}$ 19.8 0 (–94.05) (–57.8)

$\Rightarrow$ $\Delta_r H^{\Theta} = [6 \times (-94.05) + 3 \times (-57.8)] - [19.8] = -757.50$ kcal/mol.

(c) Heat of Dissociation ($\Delta_{\text{bond}} H^{\Theta}$) :

It is the amount of energy required to break one mole of bonds in a molecule (in gas phase) into gaseous atoms.

$H-H(g) \longrightarrow 2H(g)$; $\Delta_{\text{bond}} H^{\Theta} = 103$ kcal/mol

$C-C(g) \longrightarrow 2C(g)$; $\Delta_{\text{bond}} H^{\Theta} = 80$ kcal/mol

Note : (i) $\Delta_{\text{bond}} H^{\Theta}$ is always positive i.e. energy is always required to break the bond between two atoms.

(ii) Whenever a bond is formed between two atoms in gaseous state, energy is always released.

(d) Heat of Phase change :

It is the amount of energy required to change the phase of a substance under the particular conditions for the phase change.

$H_2O(s) \longrightarrow H_2O(\ell)$; $\Delta_{\text{fus}} H^{\Theta} = 6$ kJ/mol at 273 K and 1 atm

$H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta_{\text{vap}} H^{\Theta} = 40.8$ kJ/mol at 373 K and 1 atm

$CO_2(s) \longrightarrow CO_2(g)$; $\Delta_{\text{sub}} H^{\Theta} = 108$ kcal/mol at 195 K and 1 atm

Note : (i) $\Delta_{\text{fus}} H^{\Theta}$: Amount of heat required to melt one mole of a substance at a constant temperature and 1atm pressure.

(ii) $\Delta_{\text{vap}} H^{\Theta}$: Amount of heat required to vaporize one mole of a substance at a constant temperature and 1 atm pressure.

(iii) $\Delta_{\text{sub}} H^{\Theta}$: Amount of heat required to sublime one mole of a substance at a constant temperature and 1 atm pressure.

(e) Heat of Atomization ($\Delta_a H^\Theta$) :

It is the amount of energy required to break the bonds in a molecule (in gas phase) into gaseous atoms.

$$Na\,(s) \longrightarrow Na\,(g) \quad ; \quad \Delta_a H^\Theta = 108 \text{ kJ/mol}$$

$$H-H\,(g) \longrightarrow 2H\,(g) \quad ; \quad \Delta_a H^\Theta = 435 \text{ kJ/mol}$$

$$CH_4\,(g) \longrightarrow C\,(g) + 4\,H\,(g) \quad ; \quad \Delta_a H^\Theta = 1665 \text{ kJ/mol}$$

Note : (i) For a monoatomic molecule (i.e. atom) in solid phase, $\Delta_a H^\Theta$ is also called as $\Delta_{sub} H^\Theta$.

(ii) For a diatomic molecule, $\Delta_a H^\Theta$ is also called as $\Delta_{bond} H^\Theta$.

(iii) For a polyatomic molecule, it is the enery required to break all the bonds to form gaseous atoms.

(f) Average Heat of Dissociation ($\Delta_{mean,\,bond} H^\Theta$) :

It is the average amount of energy required to break one mole of bonds in a polyatomic molecule (in gas phase) into gaseous atoms.

$$CH_4\,(g) \longrightarrow C\,(g) + 4\,H\,(g) \quad ; \quad \Delta_a H^\Theta = 1665 \text{ kJ/mol}$$

Note : In general, in a polyatomic molecule, the energy required to break a bond changes in the successive bond dissociations. For example :

$$CH_4\,(g) \longrightarrow CH_3\,(g) + H\,(g) \quad ; \quad \Delta_{bond} H_1^\Theta$$

$$CH_3\,(g) \longrightarrow CH_2\,(g) + H\,(g) \quad ; \quad \Delta_{bond} H_2^\Theta$$

$$CH_2\,(g) \longrightarrow CH\,(g) + H\,(g) \quad ; \quad \Delta_{bond} H_3^\Theta$$

$$CH\,(g) \longrightarrow C\,(g) + H\,(g) \quad ; \quad \Delta_{bond} H_4^\Theta$$

Here : $\Delta_{bond} H_1^\Theta \neq \Delta_{bond} H_2^\Theta \neq \Delta_{bond} H_3^\Theta \neq \Delta_{bond} H_4^\Theta$ and $\Delta_{mean,\,bond} H^\Theta = \frac{1}{4} \Delta_a H^\Theta$

(g) Heat of Lattice($\Delta_{\text{lattice}}H^{\Theta}$) and Heat of Hydration($\Delta_{\text{hyd}}H^{\Theta}$) :

$\Delta_{\text{lattice}}H^{\Theta}$: It is the energy required to break one mole of an ionic compound into ions in their gaseous atoms.

$$NaCl(s) \longrightarrow Na^{+}(g) + Cl^{-}(g) \quad ; \quad \Delta_{\text{lattice}}H^{\Theta} = 787 \text{ kJ/mol}$$

$\Delta_{\text{hyd}}H^{\Theta}$: It is the energy released when atoms (gaseous) in one mole of an ionic compound gets hydrated.

$$Na^{+}(g) + Cl^{-}(g) \ (\equiv NaCl) \longrightarrow Na^{+}(aq.) + Cl^{-}(aq.) \ ;$$

$$\Delta_{\text{hyd}}H^{\Theta} = -783 \text{ kJ/mol}$$

Note : $\Delta_{\text{lattice}}H^{\Theta}$ is always positive and $\Delta_{\text{hyd}}H^{\Theta}$ is always negative.

(h) Heat of Solution ($\Delta_{\text{sol}}H^{\Theta}$) :

It is the change in enthalpy when one mole of a substance (solute) is completely dissolved in excess of water.

$$NaCl(s) + aq \longrightarrow Na^{+}(aq) + Cl^{-}(aq) \quad ; \quad \Delta_{\text{sol}}H^{\Theta} = 5 \text{ kJ}$$

$$HCl(g) + aq \longrightarrow HCl(aq) \quad ; \quad \Delta_{\text{sol}}H^{\Theta} = -x \text{ kJ}$$

Note : (i) $\Delta_{\text{sol}}H^{\Theta} = \Delta_{\text{lattice}}H^{\Theta} + \Delta_{\text{hyd}}H^{\Theta}$ (can be positive or negative)

(ii) Generally, when gases are dissolved, heat is evolved. In case of salts (solids), heat is absorbed except when anhydrous salts are dissolved.

(i) Heat of Ionisation ($\Delta_{\text{ionisation}}H^{\Theta}$) :

It is the amount of heat absorbed when one mole of a compound completely dissociates into ions in a solution.

$$HCN(aq) \longrightarrow H^{+}(aq) + CN^{-}(aq) \quad ; \quad \Delta_{\text{ionisation}}H^{\Theta} = +p$$

$$NH_4OH(aq) \longrightarrow NH_4^{+}(aq) + OH^{-}(aq) \quad ; \quad \Delta_{\text{ionisation}}H^{\Theta} = +q$$

(j) Heat of Neutralisation ($\Delta_{\text{neutralisation}}H^{\Theta}$) :

It is the amount of heat liberated when one gm-equivalent of acid completely neutralises by one gm-equivalent of base. In water, all strong acids (HCl, H_2SO_4, HNO_3) and strong bases [NaOH, $Ca(OH)_2$, etc] ionise completely. $\Delta_{\text{neutralisation}}H^{\Theta}$ is constant for strong acid and base neutralization and is equal to –13.7 kcal/mol = –57.27 kJ/mol.

Neutralisation can be treated as :

$$H^{+}(aq) + OH^{-}(aq) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_{\text{neutralisation}}H^{\Theta} = -13.7 \text{ kcal/mol}$$

Note : (i) $\Delta_{\text{neutralisation}}H^{\Theta}$ for weak acids (HCN, CH_3COOH, benzoic acid) and weak bases (NH_4OH, amines) is lower than that for strong acids and bases. The reason is that heat is absorbed in complete ionisation of weak acids and bases (unlike in case of strong acids and bases where no heat is required for ionisation).

(ii) $\Delta_{\text{neutralisation}}H^{\Theta}$ for the reaction between HCl and NaOH in aprotic solvents (solvents which doesn't ionizes) e.g. benzene etc. is less than –13.7 kcal/mol because HCl is a polar covalent substance and doesnt get ionizes in aprotic solvent so requires non-zero $\Delta_{\text{ionisation}}H^{\Theta}$ for neutralization.

(iii) $\Delta_{\text{neutralisation}}H^{\Theta}$ for the reaction between HF and NaOH is –16.27 kcal/mol which is greater than the expected value of –13.7 kcal/mol (obviously to be compared in terms of magnitude). The difference is due to a very high heat of hydration of flouride ion due to its small size.

Hess's Law of Constant Heat Summation

It states that change in enthalpy for any chemical reaction is constant, whether the reaction occurs in one step (directly) or in several steps (indirectly).

OR

The enthalpy change in a reaction depends upon initial and final states and is independent of the route followed to complete the reaction.

It is the direct consequence of *law of conservation of energy*. $\Delta_r H$ of overall reaction will be obtained by "*appropriate summation*" of the changes in enthalpies of various intermediate steps.

Illustrating the concept :

Find the enthalpy change for formation of $NO_2(g)$.

$$\frac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad ; \quad \Delta_f H = ?$$

Using given thermochemical equations, and applying Hess's Law :

(i) $\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \longrightarrow NO(g)$; $\Delta_r H_1 \equiv (\Delta_f H)_{NO}$

(ii) $NO(g) + \frac{1}{2} O_2(g) \longrightarrow NO_2(g)$; $\Delta_r H_2 \equiv (\Delta_c H)_{NO} \neq (\Delta_f H)_{NO_2}$

Adding two equations, we get :

$$\frac{1}{2} N_2(g) + O_2(g) \longrightarrow NO_2(g) \quad \Rightarrow \quad \Delta_r H = \Delta_r H_1 + \Delta_r H_2$$

Illustrating the concept :

Find $\Delta_r H$ *of reaction :* $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g)$

(i) $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell)$; $\Delta_r H_1 = -68.3 \text{ kcal/mol} \equiv (\Delta_f H)_{H_2O} \equiv (\Delta_c H)_{H_2}$

(ii) $H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta_r H_2 = 10.52 \text{ kcal/mol} \equiv (\Delta_{vap} H)_{H_2O}$

From Hess's Law : $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 = (-68.3) + (10.52) = -57.78$ kcal/mol

Illustration - 3 *Enthalpy of neutralisation of acetic acid by NaOH is 50.6 kJ/mol. Calculate ΔH for ionisation of CH_3COOH. Given, the heat of neutralisation of a strong acid with a strong base is –57.3 kJ/mol.*

SOLUTION :

The neutralisation of a strong acid by a strong base is represented as :

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_{\text{Neutralisation}}H^{\Theta} = -57.3 \text{ kJ / mol}$$

Now acetic acid is a weak acid, so its neutralisation is represented in two stages: First complete ionisation of weak acid and then complete neutralisation of the fully ionised acid by the base.

1. $CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H^+(aq) \quad ; \quad \Delta_{\text{Ionisation}}H^{\Theta} = ?$

2. $H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_{\text{Neutralisation}}H^{\Theta} = -57.3 \text{ kJ / mol}$

Now adding the two equations to get the equation of neutralisation ;

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(\ell) \quad ; \quad \Delta_{\text{Neutralisation}}H^{\Theta} = -50.6 \text{ kJ / mol}$$

From Hess's Law : $\Delta_{\text{Ionisation}}H^{\Theta} + (-57.3) = -50.6 \quad \Rightarrow \quad \Delta_{\text{Ionisation}}H^{\Theta} = +6.7 \text{ kJ / mol}$

Illustration - 4 *Find the heat of formation of ethyl alcohol from following data :*

$$C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta_r H = -94 \text{ kcal/mol}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_r H = -68 \text{ kcal/mol}$$

$$C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(\ell) \quad ; \quad \Delta_r H = -327 \text{ kcal/mol}$$

SOLUTION :

Always write the balanced thermodynamic equation for which $\Delta_r H$ is to be calculated.

$$2\,C(s) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(\ell) \quad ; \quad \Delta_f H = ?$$

Given :

I. $C(s) + O_2(g) \longrightarrow CO_2(g) \quad ; \quad \Delta_r H_1 = -94 \text{ kcal/mol} \equiv (\Delta_f H)_{CO_2} \equiv (\Delta_c H)_C$

II. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell) \quad ; \quad \Delta_r H_2 = -68 \text{ kcal/mol} \equiv (\Delta_f H)_{H_2O} \equiv (\Delta_c H)_{H_2}$

III. $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(\ell) ; \quad \Delta_r H_3 = -327 \text{ kcal} \equiv (\Delta_c H)_{C_2H_5OH}$

Now adding *appropriately* to get the required equation (Using *Hess's Law*) :

Operate : 2 (I) + 3(II) – (III) to get :

$$2\,C(s) + 3\,H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(\ell)$$

From Hess's Law : $\Delta_fH = 2(\Delta_rH_1) + 3(\Delta_rH_2) - \Delta_rH_3 = 2(-94) + 3(-68) - (-327) = -65$ kcal/mol

Illustration - 5 *From the following data, calculate the standard enthalpy change for the combustion of cyclopropane at 298 K* :

The enthalpy of formation of $CO_2(g)$, $H_2O(\ell)$ *and propene*(g) *are* -393.5, -285.8 *and* 20.42 *kJ mol*$^{-1}$ *respectively.*

The enthalpy of isomerisation of cyclopropane to propene is -33.0 *kJ mol*$^{-1}$.

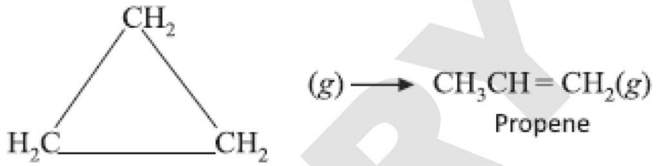
SOLUTION :

$$CH_3CH = CH_2(g) + \frac{9}{2}O_2(g) \longrightarrow 3CO_2(g) + 3H_2O(\ell) \qquad \ldots\ldots \text{(i)}$$

$$\Delta_cH^{\Theta}_{(\text{Propene})} = \left[3\Delta_fH^{\Theta}_{(CO_2)} + 3\Delta_fH^{\Theta}_{(H_2O)}\right] - \left[\Delta_fH^{\Theta}_{(\text{Propene})} + \frac{9}{2}\Delta_fH^{\Theta}_{O_2}\right]$$

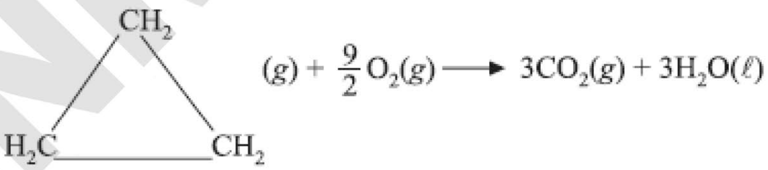
$$= 3(-393.5) + 3(-285.8) - (20.42) = -2058.32 \text{ kJ mol}^{-1}$$

To the above reaction, if we add the reaction :



$\Delta_{\text{isomerization}}H^{\Theta} = -33.0$ kJ mol^{-1}

we get :



Hence, $\Delta_cH^{\Theta}_{(\text{cyclopropane})} = (-2058.32 - 33.0)\text{ kJ mol}^{-1} = -2091.32\text{ kJ mol}^{-1}$

Heat of Reaction and Bond Energy

Let us consider that the bond energy of AB molecule is x kcal/mol.

Bond Formation : $A + B \longrightarrow A - B\ ;\ \Delta_r H = -\boldsymbol{x}$ (*Bond formation is exothermic*)

Bond Dissociation : $A - B \longrightarrow A + B\ ;\ \Delta_r H = +\boldsymbol{x}$ (*Bond dissociation is endothermic*)

During a chemical reaction, atoms and molecules are rearranged to form new molecules. During the course of chemical reaction, old bonds are broken (of reactants) and new ones are formed (of products).

A given chemical reaction can be analysed energetically into two parts :

(i) *Bond Breaking* (endothermic, $\Delta_r H > 0$)

(ii) *Bond Formation* (exothermic, $\Delta_r H < 0$)

If $\Delta_r H_1$ is the enthalpy change during bond breaking (i) and $\Delta_r H_2$ is the enthalpy change during bond formation (ii), then overall enthalpy change of the reaction ($\Delta_r H$) is given by Hess's Law:

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2$$

As discussed, $\Delta_r H$ can be calculated using Hess's law of constant heat summation or using :

$$\Delta_r H = \Sigma H_{\text{Product}} - \Sigma H_{\text{Reactants}}.$$

$\Delta_r H$ can also be theoretically calculated using bond energies in the following manner :

(i) On the reactants side, calculate the energy required to break all the bonds. If there is an element in Solid / Liquid state, also consider the energy required to convert it into gaseous state.

(ii) On the products side, calculate the energy released when products are formed. If there is an elements/compound in Solid/Liquid state, also consider the energy released when it is converted from gaseous state to the required state.

(iii) Add total energy released and absorbed to get $\Delta_r H$.

Illustration - 6 *Find $\Delta_r H$ of the reaction :* $OF_2\,(g) + H_2O\,(g) \longrightarrow O_2\,(g) + 2\,HF\,(g)$;
Average bond energies of O–F, O–H, O = O, H–F are 44, 111, 118 *and* 135 *kcal/mol respectively.*

SOLUTION :

$$OF_2\,(g) + H_2O\,(g) \longrightarrow O_2\,(g) + 2\,HF\,(g) \quad ; \quad \Delta_r H = ?$$

(i) Bond Breaking: (endothermic) : $\Delta_r H_1$

$F - O - F\,(g) \longrightarrow O\,(g) + 2\,F\,(g)\ ;\ \Delta_r H = +\,2 \times 44$ [bond energy of O – F = 44]

$H - O - H(g) \longrightarrow O\,(g) + 2\,H\,(g)\ ;\ \Delta_r H = +\,2 \times 111$ [bond energy of O – H = 111]

$\Rightarrow \quad \Delta_r H_1 = 2 \times 44 + 2 \times 111 = +\,310$ kcal.

(ii) Bond Formation: (exothermic) : $\Delta_r H_2$

$O(g) + O(g) \longrightarrow O = O(g)$; $\Delta_r H = -118$ [bond energy of $O = O = 118$]

$2[H(g) + F(g) \longrightarrow H - F(g)]$; $\Delta_r H = -2 \times 135$ [bond energy of $H - F = 135$]

$\Rightarrow \quad \Delta_r H_2 = -118 + (-2 \times 135) = -388$ kcal

Now using Hess's Law ; $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 = 310 + (-388) = -78$ kcal

Illustration - 7 *Find $\Delta_f H$ of $HCl(g)$ if bond energies of H_2, Cl_2 and HCl are* 104, 58, 103 *kcal/mol respectively.*

SOLUTION :

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g) \; ; \qquad \Delta_f H = ?$$

Now analyse the given thermochemical equation in two parts :

(i) Bond Breaking $[\Delta_r H_1]$: Endothermic Reaction

$H_2(g) \longrightarrow 2H(g)$; $\Delta_r H = 104$ kcal/mol

$Cl_2(g) \longrightarrow 2Cl(g)$; $\Delta_r H = 58$ kcal/mol

$\frac{1}{2}[H_2(g) \longrightarrow 2H(g)$; $104]$ [as we need mole of each reactant]

$\frac{1}{2}[Cl_2(g) \longrightarrow 2Cl(g)$; $58]$

$$\Rightarrow \quad \Delta_r H_1 = \frac{1}{2} \times 104 + \frac{1}{2} \times 58 = 81 \text{ kcal}$$

(ii) Bond Formation : $(\Delta_r H_2)$: Exothermic reaction

$H(g) + Cl(g) \longrightarrow HCl(g)$; $\Delta_r H = -103$ kcal (Bond energy of $HCl = 103$ kJ/mol)

$\Delta_r H_2 = -103$ kcal

Now $\Delta_r H = \Delta_f H = \Delta_r H_1 + \Delta_r H_2$ (using Hess's Law)

$\Rightarrow \quad \Delta_f H = 81 + (-103) = -22$ kcal/mol

Illustration - 8 *Calculate $\Delta_r H$ for the following homogeous gaseous reaction :*

$$CH_3COCH_3(g) + 2O_2(g) \longrightarrow CH_3COOH(g) + CO_2(g) + H_2O(g)$$

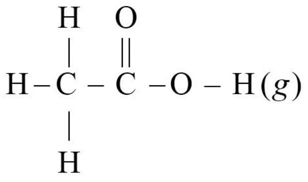
Use the data in kcal mol^{-1}. $\Delta_{bond\ C-H} = 99$; $\Delta_{bond\ C-C} = 83$; $\Delta_{bond\ C=O} = 173$;

$\Delta_{bond\ O=O} = 118$; $\Delta_{bond\ C-O} = 84$; $\Delta_{bond\ O-H} = 110$

SOLUTION :

First calculate the energy required to break all the bonds in reactants side and to convert them into gaseous atoms.

(i) $4H(g) + 2C(g) + 2O(g) \longrightarrow$



$$4H(g) + 2C(g) + 2O(g) \longrightarrow H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-H(g)$$

Energy released $= 3\Delta_{\text{Bond C-H}} + \Delta_{\text{Bond C-C}} + \Delta_{\text{Bond C=O}} + \Delta_{\text{Bond C-O}} + \Delta_{\text{Bond O-H}}$

$= 3 \times 99 + 83 + 173 + 84 + 110 = 747$ kcal

(ii) $C(g) + 2O(g) \longrightarrow O=C=O(g)$

Energy released $= 2\Delta_{\text{Bond C=O}} = 2 \times 173 = 346$ kcal

$\Rightarrow$ Total energy released = 1313 kcal

$\Rightarrow$ $\Delta_r H = 1169 + (-1313) = -144$ kcal mol^{-1}

(iii) $2H(g) + O(g) \longrightarrow H-O-H(g)$

Energy released $= 2\Delta_{\text{Bond O-H}} = 2 \times 110 = 220$ kcal

Note : (i) While calculating $\Delta_r H$ using the bond energy concept, it is important to know the structure of the molecules/compounds taking part in the reaction.

(ii) If the reaction would have been :

$CH_3COCH_3(g) + 2O_2(g) \longrightarrow CH_3COOH(g) + CO_2(g) + H_2O(\ell)$

then we also need to consider the energy released for the conversion of $H_2O(g) \longrightarrow H_2O(\ell)$

$\Delta_r H = -144 - 9.72 = -153.72$ kcal

Illustration - 9 *Compute the heat of formation of liquid methyl alcohol, using the following data (in kJ/mol) : Heat of vaporization of liquid methyl alcohol* = 38.

Heat of formation of gaseous atoms from the elements in their standard states: $H = 218$; $C = 715$; $O = 249$.

Average bond energies : $C - H = 415$; $C - O = 356$; $O - H = 463$.

SOLUTION :

The given data is as follows :

(i) $CH_3OH(\ell) \longrightarrow CH_3OH(g)$ $\qquad \Delta_r H_1^{\ominus} = 38\,\text{kJ mol}^{-1}$

(ii) $\frac{1}{2}H_2(g) \longrightarrow H(g)$ $\qquad \Delta_r H_2^{\ominus} = 218\,\text{kJ mol}^{-1}$

(iii) $C(\text{graphite}) \longrightarrow C(g)$ $\qquad \Delta_r H_3^{\ominus} = 715\,\text{kJ mol}^{-1}$

(iv) $\frac{1}{2}O_2(g) \longrightarrow O(g)$ $\qquad \Delta_r H_4^{\ominus} = 249\,\text{kJ mol}^{-1}$

(v) $C{-}H(g) \longrightarrow C(g) + H(g)$ $\qquad \Delta_r H_5^{\ominus} = 415\,\text{kJ mol}^{-1}$

(vi) $C{-}O(g) \longrightarrow C(g) + O(g)$ $\qquad \Delta_r H_6^{\ominus} = 356\,\text{kJ mol}^{-1}$

(vii) $O{-}H(g) \longrightarrow O(g) + H(g)$ $\qquad \Delta_r H_7^{\ominus} = 463\,\text{kJ mol}^{-1}$

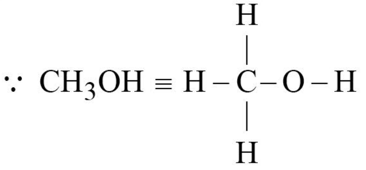
We have to calculate the enthalpy of formation of liquid methyl alcohol, i.e.,

(viii) $C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(\ell)$ $\qquad \Delta_r H_8^{\ominus} = ?$

First of all, we calculate the enthalpy of reaction :

(ix) $CH_3OH(g) \longrightarrow C(g) + 4H(g) + O(g)$; $\qquad \Delta_r H_9^{\ominus} = ?$

$$\Delta_r H_9^{\ominus} = 3\,\Delta_r H_5^{\ominus} + \Delta_r H_6^{\ominus} + \Delta_r H_7^{\ominus}$$



$$\because\ CH_3OH \equiv H - \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} - O - H$$

contains one $C - O$, one $O - H$ and three $C - H$ bonds

$$\Delta_r H_9^{\ominus} = (3 \times 415 + 356 + 463)\ \text{kJ mol}^{-1} = 2064\ \text{kJ mol}^{-1}$$

The equation (viii) can be generated as follows :

Eq. (iii) + 4 × Eq. (ii) + Eq. (iv) – Eq. (ix) – Eq. (i)

Hence, the enthalpy of reaction of equation (viii) is given as :

$$\Delta_r H_8^{\ominus} = \Delta_r H_3^{\ominus} + 4\,\Delta_r H_2^{\ominus} + \Delta_r H_4^{\ominus} - \Delta_r H_9^{\ominus} - \Delta_r H_1^{\ominus}$$

$$= (715 + 4 \times 218 + 249 - 2064 - 38)\ \text{kJ mol}^{-1} = -266\ \text{kJ mol}^{-1}$$

Illustration - 10 *The heat of formation of ethane is* –19.5 *kcal. Bond energies of H – H, C – H and C – C bonds are* 104.2, 99.0 *and* 80.0 *kcal/mol respectively. Calculate the heat of atomisation of graphite.*

SOLUTION :

$\Delta_f H$ of ethane (C_2H_6) = –19.5 kcal/mol

$2\,C\,(s) + 3\,H_2\,(g) \longrightarrow C_2H_6\,(g)$; $\Delta_f H = -19.5$ kcal/mol

Let the heat of atomisation is x kcal/mol

Bond Breaking : ($\Delta_r H_1$)

$2[C\,(s) \longrightarrow C(g);\ +x]$

$3[H_2\,(g) \longrightarrow 2\,H\,(g)\,;\ +104.2]$

$\Delta_r H_1 = 2x + 312.6$

Bond Formation : ($\Delta_r H_2$)

$1[C\,(g) + C\,(g) \longrightarrow C-C\,(g)\ ;\ -80]$

$6[C\,(g) + H\,(g) \longrightarrow C-H\,(g)\,;\ -99]$

$\Delta_r H_2 = (-80) + (6 \times -99) = -674$

From Hess's Law : $\Delta_f H = \Delta_r H_1 + \Delta_r H_2$

$-19.5 = (2x + 312.6) - 674 \quad \Rightarrow \quad x = 171$ kcal.

Illustration - 11 *Using the data given below (all values are in kcal/mol at 25°C), calculate the bond energies of C–C and C–H bonds.*

$\Delta_c H^{\ominus}_{(ethane)} = -372.0$; $\Delta_c H^{\ominus}_{(propane)} = -530.0$; $\Delta_a H^{\ominus}_{C(Graphite)} = 172.0$;

$\Delta_{\text{bond}} H^{\ominus}_{H-H} = 104.0$; $\Delta_f H^{\ominus}_{(H_2O)} = -68.0$; $\Delta_f H^{\ominus}_{(CO_2)} = -94.0$

SOLUTION :

From the data given for heats of combustion for ethane and propane, we can calculate the heats of formation of two compounds (C_2H_6 and C_3H_8) as follows :

(a) Writing the equation for combustion of ethane:

$$C_2H_6\,(g) + \frac{7}{2}O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 3\,H_2O\,(\ell) \quad ; \quad \Delta_c H^{\ominus} = -372.0$$

From definition of $\Delta_r H$ of a reaction : $\Delta_r H = \Sigma H_{\text{Products}} - \Sigma H_{\text{Reactants}}$

The enthalpy of a compound is the enthalpy of formation of that compound at standard conditions (i.e. $\Delta_f H^{\ominus}$).

$$\Delta_c H^{\ominus} = \left[2\Delta_f H^{\ominus}_{(CO_2)} + 3\,\Delta_f H^{\ominus}_{(H_2O)}\right] - \left[\Delta_f H^{\ominus}_{(C_2H_6)} + \frac{7}{2}\,\Delta_f H^{\ominus}_{(O_2)}\right]$$

Note that $\Delta_f H^{\ominus}_{(O_2)} = 0$ (as enthalpy of formation of an element in standard state is taken as zero).

$\Rightarrow \quad -372 = 2 \times (-94) + 3 \times (-68) - \Delta_f H^{\ominus}_{(C_2H_6)}$

$\Rightarrow \quad \Delta_f H^{\ominus}_{(C_2H_6)} = -20$ kcal/mol

(b) Writing the equation for combustion of propane :

$$C_3H_8\,(g) + 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(\ell) \quad ; \quad \Delta_c H^{\ominus} = -530.0$$

From definition of $\Delta_r H$ of a reaction : $\Delta_r H = \Sigma H_{\text{Products}} - \Sigma H_{\text{Reactants}}$

$$\Delta_c H^{\ominus} = \left[3\,\Delta_f H^{\ominus}_{(CO_2)} + 4\Delta_f H^{\ominus}_{(H_2O)}\right] - \left[\Delta_f H^{\ominus}_{(C_3H_8)} + 5\Delta_f H^{\ominus}_{(O_2)}\right]$$

$\Rightarrow \quad -530 = 3 \times (-94) + 4 \times (-68) - \Delta_f H^{\ominus}_{(C_3H_8)}$

$\Rightarrow \quad \Delta_f H^{\ominus}_{(C_3H_8)} = -24$ kcal / mol

Calculations of bond energies :

Let the bond energy of C – C bond = x kcal mol^{-1} and the bond energy of C – H bond = y kcal mol^{-1}

(a) *For ethane*, heat of formation is given as :

$$2\,C(s) + 3\,H_2\,(g) \longrightarrow C_2H_6(g)\,; \quad \Delta_f H^{\ominus} = -20 \text{ kcal mol}^{-1}$$

Bond breaking ($\Delta_r H_1$) :	**Bond formation ($\Delta_r H_2$) :**
$2[\,C(s) \longrightarrow C(g)\;;\,+172\,]$	$1[\,C\,(g) + C\,(g) \longrightarrow C-C\,(g)\,;\,-x\,]$
$3[\,H_2(g) \longrightarrow 2H(g)\,;\,+104\,]$	$6[\,C\,(g) + H\,(g) \longrightarrow C-H\,(g)\,;\,-y\,]$
$\Rightarrow \Delta_r H_1 = 2 \times 172 + 3 \times 104 = 656$	$\Rightarrow \Delta_r H_2 = -(x + 6y)$

$\Rightarrow \quad \Delta_f H^{\ominus}$ = heat absorbed + heat released = $\Delta_r H_1 + \Delta_r H_2$

$\Rightarrow \quad -20 = 656 - (x + 6y) \quad \Rightarrow \quad x + 6y = 676 \qquad$ . . . . (i)

(b) *For propane*, heat of formation is given as :

$$3\,C(s) + 4\,H_2(g) \longrightarrow C_3H_8(g)\;; \qquad \Delta_r H^\ominus = -24 \text{ kcal mol}^{-1}$$

Bond breaking ($\Delta_r H_1$) :

$3[\,C(s) \longrightarrow C(g) \quad ; +172\,]$

$4[\,H_2(g) \longrightarrow 2H(g)\,; +104\,]$

$\Delta_r H_1 = 3 \times 172 + 4 \times 104 = 932$

Bond formation ($\Delta_r H_2$) :

$2[\,C(g) + C(g) \longrightarrow C - C(g)\,;\ -x\,]$

$8[\,C(g) + H(g) \longrightarrow C - H(g)\,;\ -y\,]$

$\Rightarrow \quad \Delta_r H_2 = -\,(2x + 8y)$

$$\Rightarrow \quad \Delta_f H^\ominus = \Delta_r H_1 + \Delta_r H_2$$

$$\Rightarrow \quad -24 = 932 - (2x + 8y) \qquad \Rightarrow \qquad x + 4y = 478 \qquad \ldots\ldots \text{(ii)}$$

Solving (i) and (ii), we get $x = 82$ and $y = 99$.

$\Rightarrow$ Bond energy of C – C bond = 82 kcal mol^{-1} and C – H bond = 99 kcal mol^{-1}

Born Haber's Cycle

The energy binding ions together in a crystal is called as *lattice energy* ($\Delta_{\text{Lattice}}H^\ominus$). Lattice energy is defined as the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state which means $\Delta_{\text{Lattice}}H^\ominus$ is +ve i.e.,

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta_{\text{Lattice}}H^\ominus = +790 \text{ kJ mol}^{-1}$$

These crystal lattice energies cannot be measured directly. By applying Hess's Law to a series of elementary processes starting with Na (s) and Cl_2 (g) and ending with formation of NaCl(s), $\Delta_{\text{Lattice}}H^\ominus$ can be calculated. Such a sequence of reactions for ionic compounds is called as *Born-Haber Cycle*. The concept is illustrated below by taking the formation of NaCl(s).

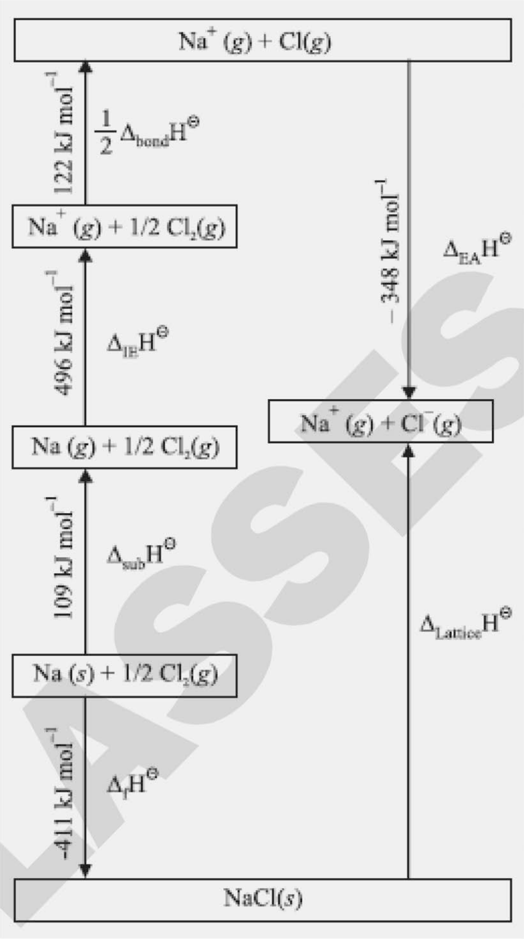
The heat of formation of sodium chloride can be calculated from bond energies very easily.

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s) \qquad \Delta_f H^\ominus = -411 \text{ kJ mol}^{-1}$$

The following sequences can give the above equation :

1. Sublimation of one mole of Na(s) :

$$Na(s) \longrightarrow Na(g) \qquad \Delta_{\text{sub}}H^\ominus = +109 \text{ kJ mol}^{-1}$$



2. Dissociation of half mole of Cl_2 :

$$\frac{1}{2}\ Cl_2(g) \longrightarrow Cl(g)$$

$$\frac{1}{2}\Delta_{Bond}H^\ominus = +122\ \text{kJ mol}^{-1}$$

(Bond energy of Cl_2 is $\Delta_{Bond}H^\ominus$

= 244 kJ/mole)

3. Ionisation of one mole of Na atoms :

$$Na(g) \longrightarrow Na^+(g) + 1e^-$$

$$\Delta_{IE}H^\ominus = +\ 496\ \text{kJ mol}^{-1}$$

(First ionisation energy of Na atoms is 496 kJ/mole)

4. Addition of one mole of electrons to one mole of chlorine atoms:

$$Cl(g) + 1e^- \longrightarrow Cl^-(g)$$

$$\Delta_{EA}H^\ominus = -\ 348\ \text{kJ mol}^{-1}$$

(Electron affinity of chlorine is 348 kJ/mole)

(*Electron affinity is the energy released, so ΔH is negative*).

5. Condensation of gaseous ions to form one mole of solid NaCl :

This can not be calculated directly.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \quad \Delta_r H^\ominus = -\Delta_{Lattice}H^\ominus$$

The summation of the above five reactions and their ΔH values allows us to calculate the value of $\Delta_{Lattice}H^\ominus$.

$$\Delta_f H^\ominus\ (-411) = \Delta_{sub}H^\ominus\ (+109\text{kJ}) + \frac{1}{2}\Delta_{Bond}H^\ominus\ (+122\text{kJ}) + \Delta_{IE}H^\ominus\ (+496\text{kJ}) + \Delta_{EA}H^\ominus$$

$$(-348\text{kJ}) - \Delta_{Lattice}H^\ominus$$

$$\Rightarrow \quad \Delta_{Lattice}H^\ominus = +790\ \text{kJ/mol of solid NaCl.}$$

Note : The crystal lattice is a measure of the stability of an ionic solid. The more negative its value, the more energy is released in the hypothetical reaction in which a mole of ionic solid is formed from its constituent ions in the gaseous state.

Illustration - 12 *Find the electron affinity of chlorine from the following data (in kcal/mol).*
Enthalpy of formation of LiCl is –97.5 ; Lattice energy of LiCl = 197.7 ; Dissociation energy of chlorine = 57.6 ; Sublimation enthalpy of Lithium = 38.3 ; Ionisation energy of Lithium = 123.8

SOLUTION :

For a ionic compound of type LiCl :

$$\Delta_{\text{Lattice}}H^{\ominus}_{\text{LiCl}} = \Delta_{\text{EA}}H^{\ominus}_{\text{Cl}} - \Delta_{\text{f}}H^{\ominus}_{\text{LiCl}} + \frac{1}{2}\Delta_{\text{bond}}H^{\ominus}_{\text{Cl2}} + \Delta_{\text{sub}}H^{\ominus}_{\text{Li}} + \Delta_{\text{IE}}H^{\ominus}_{\text{Li}}$$

$$197.7 = \Delta_{\text{EA}}H^{\ominus}_{\text{Cl}} - (-97.5) + \frac{1}{2}\times 57.6 + 38.3 + 123.8$$

$$\Rightarrow \quad \Delta_{\text{EA}}H^{\ominus}_{\text{Cl}} = -\,90.7\text{ kcal / mol}$$

Relation between Δ_rH and Δ_rU — Section - 6

Enthalpy (H) and Internal Energy (U) are related as :

$$H = U + PV$$

$$\Rightarrow \quad \Delta H = \Delta U + \Delta(PV)$$

or $\quad dH = dU + d(PV)$

Now, for a reaction, we can write : $\Delta_r H = \Delta_r U + P\Delta V$

[Chemical reactions occur at constant T and P]

or $\quad \Delta_r H = \Delta_r U + \Delta n_g RT$

where $\Delta n_g = \sum(n_g)_{\text{products}} - \sum$ [illegible] nge in the number of gaseous moles

Illustration - 13 *Find the sign of $\Delta_r H - \Delta_r U$ for the following reactions :*

(i) $H_2(g) + Cl_2(g) \longrightarrow HCl(g)$ (ii) $N_2(g) + O_2(g) \longrightarrow NO_2(g)$

(iii) $PH_3(g) \longrightarrow P_4(s) + H_2(g)$ (iv) $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow CO_2(g) + H_2O(\ell)$

SOLUTION :

First, balance each reaction :

(i) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

(ii) $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$

(iii) $4PH_3(g) \longrightarrow P_4(s) + 6H_2(g)$

(iv) $C_2H_6(g) + \frac{7}{2} O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$

Now, Use : $\Delta_r H - \Delta_r U = \Delta n_g RT$ and $\Delta n_g = \sum (n_g)_{\text{products}} - \sum (n_g)_{\text{reactants}}$

$\Rightarrow$ If $\Delta n_g > 0$, $\Delta_r H - \Delta_r U > 0$;

If $\Delta n_g < 0$, $\Delta_r H - \Delta_r U < 0$;

If $\Delta n_g = 0$, $\Delta_r H - \Delta_r U = 0$

(i) $\Delta n_g = 2 - (1 + 1) = 0$ (ii) $\Delta n_g = 2 - (1 + 2) = -1$

(iii) $\Delta n_g = (6 + 0) - 4 = 2$

(iv) $\Delta n_g = (2 + 0) - \left(1 + \frac{7}{2}\right) = -\frac{5}{2}$ [***Note*** : For $H_2O(\ell)$, $n_g = 0$]

Illustration - 14 *The enthalpies of combustion of carbon and carbon monoxide in excess of oxygen at 298 K and constant pressure are –393.5 kJ/mol and –283.0 kJ/mol respectively. Calculate the heat of formation of carbon monoxide at constant volume.*

SOLUTION :

Heat change at constant pressure means enthalpy change ($\Delta_r H = q_p$)

Heat of formation of CO is written as : $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$; $\Delta_f H^\ominus = ?$

Now we have :

I. $C(g) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_c H_1^\ominus = -393.5 \text{ kJ / mol}$

II. $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$; $\Delta_c H_2^\ominus = -283 \text{ kJ / mol}$

Adding appropriately (i.e., I – II), we get ; $C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g) \quad ; \quad \Delta_f H^{\ominus}$

From Hess's Law : $\Delta_f H^{\ominus} = \Delta_c H_1^{\ominus} - \Delta_c H_2^{\ominus}$

$$\Delta_f H^{\ominus} = -393.5 - (-283) = -110.5 \text{ kJ/mol}$$

Now, calculation of the heat of formation at constant volume means that we have to calculate change in internal energy (i.e. $\Delta_r U$).

Using : $\Delta_r H = \Delta_r U + P\Delta V$ [For a chemical reaction]

$= \Delta_r U + \Delta n_g RT$ [Δn_g = gaseous moles of products – gaseous moles of reactant]

$\Rightarrow \quad \Delta_r U = \Delta_r H - \Delta n_g RT$

Now putting the values :

$\Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$ $\quad T = 298$ K $\quad R = 8.314$ J/K/mol. $\quad \Delta_f H^{\ominus} = -110.5$ kJ/mol

$$\Rightarrow \quad \Delta_f U^{\ominus} = -110.5 - \frac{1}{2} \times 8.314 \times 298 \times 10^{-3} = -111.7 \text{ kJ/mol}$$

Illustration - 15 *Standard enthalpy of formation of $C_3H_7NO_2(s)$, $CO_2(g)$ and $H_2O(\ell)$ are –133.6, – 94.0 and – 68.3 kcal/mol respectively. Standard enthalpy of combustion of $CH_4(g)$ at 25°C is – 212.8 kcal/mol.*

Calculate $\Delta_r H^{\ominus}$ for the reaction: $2CH_4(g) + CO_2(g) + \frac{1}{2} N_2(g) \longrightarrow C_3H_7NO_2(s) + \frac{1}{2} H_2(g)$

Also calculate heat of reaction at constant volume for combustion of $C_3H_7NO_2(s)$.

SOLUTION :

$$2CH_4(g) + CO_2(g) + \frac{1}{2} N_2(g) \longrightarrow C_3H_7NO_2(s) + \frac{1}{2} H_2(g) : \quad \Delta_r H^{\ominus} = ?$$

To calculate $\Delta_r H^{\ominus}$ of the above reaction, we need to find out the $\Delta_f H^{\ominus}$ for CH_4 as :

Given : $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell) : \quad \Delta_c H^{\ominus} = -212.8$ kcal/mol

Using the definition of $\Delta_r H$, we have :

$$\Delta_r H^\ominus = [\Delta_f H^\ominus_{(CO_2)} + 2\Delta_f H^\ominus_{(H_2O)}] - [\Delta_f H^\ominus_{(CH_4)} + 2\Delta_f H^\ominus_{O_2}] \qquad [\text{Note}: \Delta_f H^\ominus_{(O_2)} = 0]$$

$$\Rightarrow \quad -212.8 = [-94.0 + 2(-68.3)] - \Delta_f H^\ominus_{(CH_4)}$$

$$\Rightarrow \quad \Delta_f H^\ominus_{(CH_4)} = -17.8 \text{ kcal/mol}$$

Now find the $\Delta_f H^\ominus$ of the required equation using $\Delta_f H^\ominus_{(CH_4)}$.

$$\Delta_r H^\ominus = [\Delta_f H^\ominus_{(C_3H_7NO_2)} + 0] - [2 \times \Delta_f H^\ominus_{(CH_4)} + \Delta_f H^\ominus_{(CO_2)}]$$

$$\Rightarrow \quad \Delta_r H^\ominus = (-133.6) - 2(-17.8) - (-94.0) = -4.0 \text{ kcal / mol}$$

Now calculate

$$\Delta_c H^\ominus_{(C_3H_7NO_2)}: \quad C_3H_7NO_2(s) + \frac{15}{4} O_2(g) \longrightarrow 3CO_2(g) + \frac{1}{2} N_2(g) + \frac{7}{2} H_2O(\ell)$$

$$\Delta_c H^\ominus_{(C_3H_7NO_2)} = 3(-94.0) + \frac{7}{2}(-68.3) - (-133.6) = -387.45 \text{ kcal / mol}$$

Find $$\Delta_r U^\ominus = \Delta_r H^\ominus - \Delta n_g RT = -387.45 - \left(-\frac{1}{4}\right) \times 2 \times 10^{-3}(298)$$

$$= -387.6 \text{ kcal / mol} \qquad \left[\Delta n_g = \left(3 + \frac{1}{2}\right) - \frac{15}{4}\right]$$

Illustration - 16 *From $N_{avogardo}$ atoms of an element A, when half the atoms transfer one electron to another atom, 405 kJ/mol of energy was found to be consumed. An additional energy of 745 kJ was further required to convert all the A^- ions to A^+. Calculate the ionisation energy and the electron affinity of atom A in eV.*

SOLUTION :

Let I.E. be x eV/atom and E.A. be y eV/atom (magnitudes)

$A \longrightarrow A^+ + e^-$; $\Delta_r H = \text{I.E.} = x$ $\qquad$ $A + e^- \longrightarrow A^-$; $\Delta_r H = \text{E.A.} = -y$

I : Energy absorbed in eV $= \dfrac{405 \times 10^3}{1.6 \times 10^{-19}}$

$$\Rightarrow \quad \frac{405 \times 10^3}{1.6 \times 10^{-19}} = x \times \frac{6.02 \times 10^{23}}{2} - y \times \frac{6.02 \times 10^{23}}{2} \qquad \text{....(i)}$$

$A^- \longrightarrow A \longrightarrow A^+$

II : Energy absorbed in eV $= \dfrac{745 \times 10^3}{1.6 \times 10^{-19}}$

$$\Rightarrow \quad \frac{745 \times 10^3}{1.6 \times 10^{-19}} = x \times \frac{6.02 \times 10^{23}}{2} + y \times \frac{6.02 \times 10^{23}}{2} \qquad \text{. . . . (ii)}$$

Solve for IE and EA using (i) and (ii), IE = 11.93 eV/atom and EA = 3.52 eV/atom (Magnitudes)

Illustration - 17 *In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre/hour of CH_4 and 6x litre/hour of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output, what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Heats of combustion : CH_4 = 809 kJ/mol;*

C_4H_{10} = 2878 kJ /mol.

SOLUTION :

First calculate the amount of energy required in the burner per hour using methane as follows :

$$\Delta_c H^{\ominus}{}_{CH_4} = 809 \text{ kJ mol}^{-1} \equiv \frac{809}{24.48} \text{ kJ / L (at 25°C)}$$

$\Rightarrow$ 1 mol CH_4 ($\equiv$ 24.48 L at 25°C) on combustion produces 809 kJ

$\Rightarrow$ x L/hr CH_4 on combustion produces energy $= \dfrac{x}{24.48} \times 809$ kJ / hr

Now, this much energy will be required by burning of butane and we can find its rate of consumptiom as :

$$\Delta_c H^{\ominus}{}_{C_4H_{10}} = 2878 \text{ kJ mol}^{-1} \equiv \frac{2878}{24.48} \text{ kJ / L (at 25°C)}$$

$\Rightarrow$ Required Rate of combustion of propane $= \dfrac{\dfrac{x}{24.48} \times 809}{\dfrac{2878}{24.48}} \dfrac{\text{L}}{\text{hr}} = 0.28x$ L / hr

$$C_4H_{10}(g) + \frac{13}{2} O_2 (g) \longrightarrow 4CO_2(g) + 5H_2O(\ell)$$

$\Rightarrow$ 1 mol $CH_4 \equiv \dfrac{13}{2}$ mol O_2 (theoretically)

$\Rightarrow$ $\left(3 \times \frac{13}{2}\right)$ mol of O_2 is required/mol of CH_4 (practically) [Given]

$\Rightarrow$ rate of O_2 per hour $= (0.28x) \times \left(\frac{39}{2}\right) = (5.48\,x)$ L O_2

Bomb Calorimeter

Calorimetry is study of heat transfer during physical and chemical processes. A calorimeter is device for measuring energy transferred as heat. The most common device for measuring ΔU is the adiabatic bomb calorimeter, shown in figure (figure 1 & 2). The inner vesel or the 'bomb' (figure 2) and its cover are made of strong steel coated inside with gold or platinum or some other non-oxidisable material. The cover can be fitted tightly to the vessel by means of a metallid screwed down on a lead washer. A weighed amount of the substance is taken in a platinum cup C which is supported on a rod R.

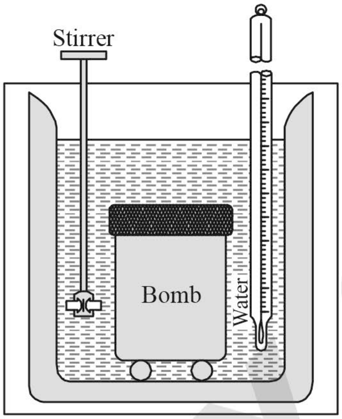


Figure 1 : The Bomb Calorimeter

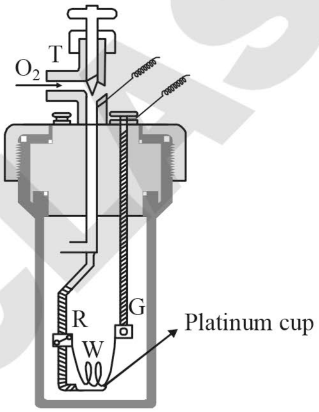


Figure 2 : The Bomb

A thin platinum wire W is connected between the rods R and G as shown. This serves to initiate the combustion when heated electrically. The bomb is tightly closed and oxygen introduced through the inlet tube T unit a pressure of about 20 – 25 atmospheres is attained. The bomb is then lowered in water placed in a double jacketed and polished metallic calorimeter so as to minimise error due to radiation. The arrangement ensures that there is no net loss of heat from the calorimeter to the surroundings (the bath) and hence that the process is adiabatic. A mechanical stirrer is provided as shown. When the temperature of the water become steady, the substance of inginited by calorimeter is noted after every minute by means of a Beckmann thermometer graduate to read up to hundredth of a degree. The final temperature when corrected for the radiation error in the usual way, minus the initial temperature, gives the rise of temperature. The heat capacity of the calorimeter system, called the calorimeter constant, C, is obtained by burning a known mass of a substance of known enthalpy of combustion. For this purpose, usually benzoic acid of high grade purity is taken. Its q_v which has been very carefully measured in taken as -3226.7 kJ mol^{-1}. Suppose the thermal capacity of the calorimeter system including water is C and θ is the change in temperature produced by burning a quantity m of the given substance of molar mass M. Then, the constant volume heat of combustion, q_v of the substance is given by C × q × M/m. The enthalpy of combustion q_p is then obtianed with the help of the equation $q_p = q_v + \Delta n_g RT$.

Illustrating the concepts :

(i) 0.50 of benzoic acid was subjected to combustion in a bomb calorimeter when the temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the enthalpy of combustion of benzoic acid. The ΔT calorimeter constant was found to be 23.85 kJ K^{-1}.

$$q_v = C \times q \times M/m$$

$$= 23.85 \text{ kJ K}^{-1} \times 0.55 \text{ K} \times 122 \text{ g mol}^{-1} / 0.50 \text{ g}$$

$$= 3200.7 \text{ mol}^{-1}$$

$$= -3200.7 \text{ kJ mol}^{-1}$$ (Heat of combustion has alwas a negative sign)

$$C_6H_5COOH(s) + \frac{15}{2}O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(\ell)$$

We know that $q_p = q_v + \Delta n_g RT$; $\Delta n = 7 - 7.5 = -0.5$

$$q_p = -3200.7 \text{ kJ mol}^{-1} + (-0.5)(8.314 \times 10^{-3} \text{kJ K}^{-1}\text{mol}^{-1})(298\text{K})$$

$$= -3201.9 \text{ kJ mol}^{-1}$$

(ii) Explain why the following statement, made by a student doing an experiment on bomb calorimeter, is wrong : "ΔH = ΔU + PΔV. Since in the experiment, ΔV = 0, hence, ΔH = ΔU."

The error is due to the fact that the student has applied the equation ΔH = ΔU + PΔV, which holds at constant pressure, to a process which occurs at constant volume.

We know that $H = U + PV$

$\therefore$ $\Delta H = \Delta U + \Delta(PV) = \Delta U + P\Delta V + V\Delta P$

For a constant pressure process, ΔP = 0 so that ΔH = ΔU + PΔV

However, for a constant volume process, ΔV = 0 so that ΔH = ΔU + VΔP

We many meantion here that a calorimeter for studying processes at constant pressure, called an isobaric calorimeter is also available commercially. A simple example is thermally insulated vessel open to the atmosphere ; the heat released in the reaction monitored by measuring the change in temperature of the contents. For a combustion reaction, an adiabatic flame calorimeter can be used to measure ΔT when a given amount of substance burns in oxygen.

Enthalpy of Polymerization :

The difference between the enthalpy of one mole of monomer and the enthalpy of the products of the polymerization reaction. Addition polymerizations are exothermic, values ranging from about 35 to 100 kJ/mol

Let us consider an example of polythene.

$$n\left(H_2C=CH_2\right)\longrightarrow..........-CH_2-CH_2-CH_2-CH_2-............$$

$$\Delta H_{(\text{Per mole})}=\text{B.E. of Reactants}-\text{B.E. of Products}$$

$$(\text{B.E. of } C=C+4\times\text{ B.E. of } C-H)-(2\times\text{ B.E. of } C-C+4\times\text{ B.E. of } C-H)$$

Same logic can also be used in following reactions as well

$$nN_{2(g)}+nH_{2(g)}\longrightarrow\left(NH-NH\right)_{n(g)}$$

$$n(H_3C-C\equiv C-CH_3)_{(g)}\longrightarrow\left(CH_2-CH=CH-CH_2\right)_{n(g)}$$

CALCULATING RESONANCE ENERGY

Resonance energy, as we know, is the difference in energy between resonance hybrid and the canonical form of the compound. It can be easily calculated using the following key points :

(i) If the resonance hybrid is more stable than the canonical forms, resonance energy is negative otherwise positive.

(ii) Simply figure out, which of the resonance hybrid and the canonical form is more stable based on the $\Delta_r H$ values as explained :

(a) $\Delta_f H^{\ominus}$ **:** More negative is $\Delta_f H^{\ominus}$, more is the stability as this means when compound is formed, energy is getting lost to attain lower energy than the reactants.

(b) $\Delta_c H^{\ominus}$ or $\Delta_{\text{Hydrogenation}} H^{\ominus}$ **:** More negative value in this case means less stability as more heat released means this compound is more reactive.

Note : In **(a)**, the compound under analysis is the product whereas in **(b)**, that compound is the reactant.

(iii) Now, calculate ΔH for the theoretical (canomical) and actual (resonance hybrid) compound and calculate the difference between the two to get resonance energy.

Illustration - 18 *The standard molar enthalpies of formation of cyclohexane(ℓ) and benzene(ℓ) at 25°C are –156 and +49 kJ/mole respectively. The standard enthalpy of hydrogenation of cyclohexene(ℓ) at 25°C is –119 kJ/mole. Use this data to estimate the magnitude of the resonance energy of benzene.*

SOLUTION :

Given : $C_6H_{10}(\ell) + H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_{\text{Hydrogenation}}H^{\ominus} = -119$ kJ/mole

Find the actual heat of hydrogenation of benzene from Hess's law as follows :

1. $6C(s) + 6H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_f H^{\ominus} = -156$ kJ/mole
2. $6C(s) + 3H_2(g) \longrightarrow C_6H_6(\ell)$; $\Delta_f H^{\ominus} = +49$ kJ/mole

$C_6H_6(\ell) + 3H_2(g) \longrightarrow C_6H_{12}(\ell)$; $\Delta_{\text{Hydrogenation}}H^{\ominus}$

$\Rightarrow$ $(\Delta_{\text{Hydrogenation}}H^{\ominus})_{\text{Actual}} = -156 - 49 = -205$ kJ/mole

[*Note* : $\Delta_{\text{Hydrogenation}}H^{\odot}$ is always negative]

$$\text{Now,} \begin{pmatrix}\text{hypothetical heat of}\\ \text{hydrogenation of benzene}\end{pmatrix} \equiv \begin{pmatrix}\text{heat of hydrogenation of}\\ \text{cyclo hexatriene}\end{pmatrix}$$

$$\equiv 3 \times \begin{pmatrix}\text{heat of hydrogenation}\\ \text{of cyclohexane}\end{pmatrix}$$

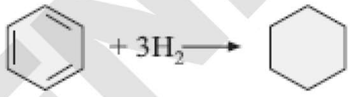
$$= 3 \times (-119) = -357 \text{ kJ/mole}$$

Here, we have assumed that there are only 3 double bonds in benzene (kekule's structure) and in hydrogenating it, the energy obtained will be roughly 3 times of hydrogenating cyclohexene.

$\Rightarrow$

$(\Delta_{\text{Hydrogenation}}H^{\ominus})_{\text{Cyclohexene}}$

and



$(\Delta_{\text{Hydrogenation}}H^{\ominus})_{\text{Theoretical Benzene}} = 3 \times (\Delta_{\text{Hydrogenation}}H^{\ominus})_{\text{Cyclohexene}}$

Clearly, heat of hydrogenation for theoretical benzene is more negative and thus, it is less stable. So, Resonance energy should be negative (since actual benzene is more stable).

$\Rightarrow$ Resonance energy = –357 – (–205) = –152 kJ/mole of benzene

Illustration - 19 *Calculate the resonance energy of isoprene (C_5H_8) from the data given. Standard Heats of combustion of isoprene, carbon and water are 3186, 393.5 and –285.83 kJ/mole respectively. Bond energies of C = C, C – C, C – H and H – H bonds are 615, 348, 413, 435.8 kJ/mole respectively. Standard Heat of sublimation of graphite is 718.3 kJ/mole.*

SOLUTION :

Calculate $\Delta_f H^\ominus$ of isoprene from its heat of combustion (This will give the value for the actual isoprene existing in nature).

$$5C\,(s) + 4H_2\,(g) \longrightarrow C_5H_8\,(g) \quad ; \quad \Delta_f H^\ominus = ?$$

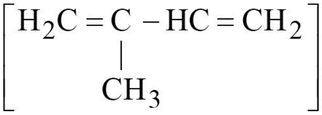
1. $C_5H_8\,(g) + 7\,O_2\,(g) \longrightarrow 5\,CO_2\,(g) + 4\,H_2O\,(\ell)$; $\Delta_r H_1^\ominus = -3186$ kJ/mole
2. $C(s) + O_2\,(g) \longrightarrow CO_2\,(g)$; $\Delta_r H_2^\ominus = -393.5$ kJ/mole
3. $H_2\,(g) + 1/2\,O_2\,(g) \longrightarrow H_2O\,(\ell)$; $\Delta_r H_3^\ominus = -285.83$ kJ/mole

Now operating 5(2) + 4(3) – 1 to get the equation of heat of formation.
From Hess's Law we have :

$$\Delta_f H^\ominus = 5\Delta_r H_2^\ominus + 4\Delta_r H_3^\ominus - \Delta_r H_1^\ominus$$

$$\Rightarrow \quad \Delta_f H^\ominus = 5(-393.5) + 4(-285.83) - (-3186) \quad \Rightarrow \quad (\Delta_f H^\ominus)_{\text{actual}} = 75.18\ \text{kJ / mole}$$

Now calculate heat of formation using the bond energies and structure of isoprene.



$$\left[\begin{array}{c} H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} - HC = CH_2 \end{array}\right]$$

Note : Data calculations from the bond energy concept is always theoretical.

1. Bond Breaking : (ΔH_1)

   $5\,[\,C(s) \longrightarrow C(g)\ ;\ +718.3\,]$

   $4\,[\,H_2(g) \longrightarrow 2H\ ;\ +435.8\,]$

   $\Rightarrow \quad \Delta H_1 = 5 \times 718.3 + 4 \times 435.8$

   $= +\,5334.7$ kJ

2. Bond Formation : (ΔH_2)

   $8[\,C + H \longrightarrow C - H\ ;\ -413\,]$

   $2[\,C + C \longrightarrow C - C\ ;\ 348\,]$

   $2[\,C + C \longrightarrow C = C\ ;\ -615\,]$

   $\Rightarrow \quad \Delta H_2 = -(8 \times 413 + 2 \times 348 + 2 \times 615)$

   $= -5230$ kJ

From Hess's Law : $(\Delta_f H^{\ominus})_{\text{Theoretical}} = \Delta H_1 + \Delta H_2$

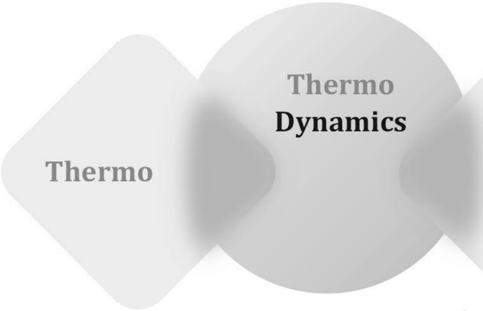
$$(\Delta_f H^{\ominus})_{\text{Theoretical}} = 5334.7 + (-5230) = 104.7 \text{ kJ}$$

$\Rightarrow$ Resonance Energy = 75.18 – 104.7 = –29.52 kJ

Introduction

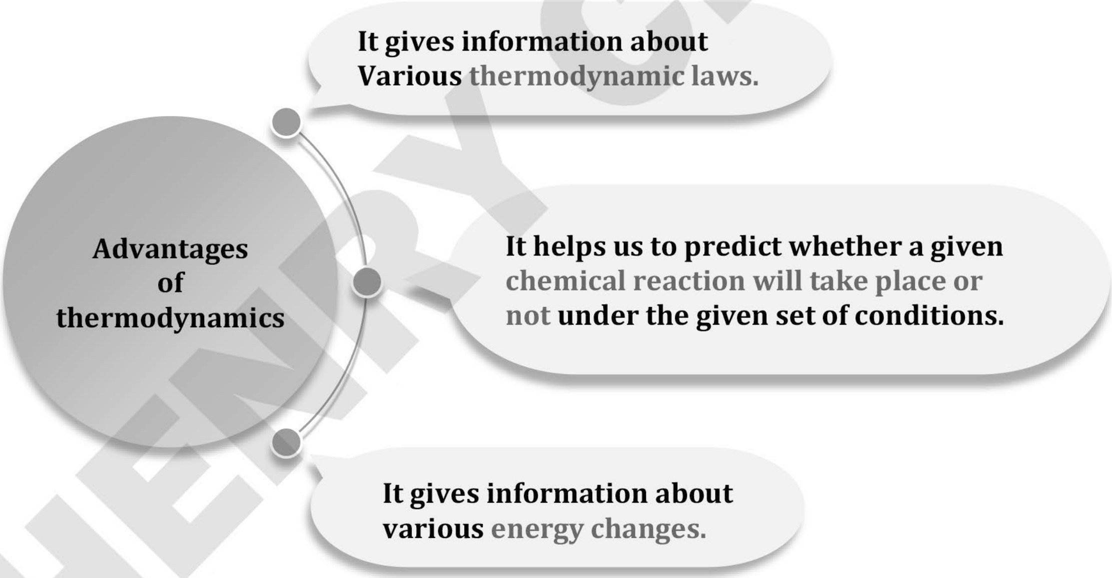
Thermo (Heat/energy) + Dynamics (Flow/motion)

Thermodynamics is the branch of science which deals with the energy changes taking place in all physical and chemical processes but **Chemical thermodynamics** is the branch of thermodynamics which deals with the study of energy changes taking place in chemical processes.



Thermo is derived from a Greek word "Thermes" means Heat

Dynamics is derived from a Greek word "Dynamikos" means study of motion.



Advantages of thermodynamics

- **It gives information about Various thermodynamic laws.**
- **It helps us to predict whether a given chemical reaction will take place or not under the given set of conditions.**
- **It gives information about various energy changes.**

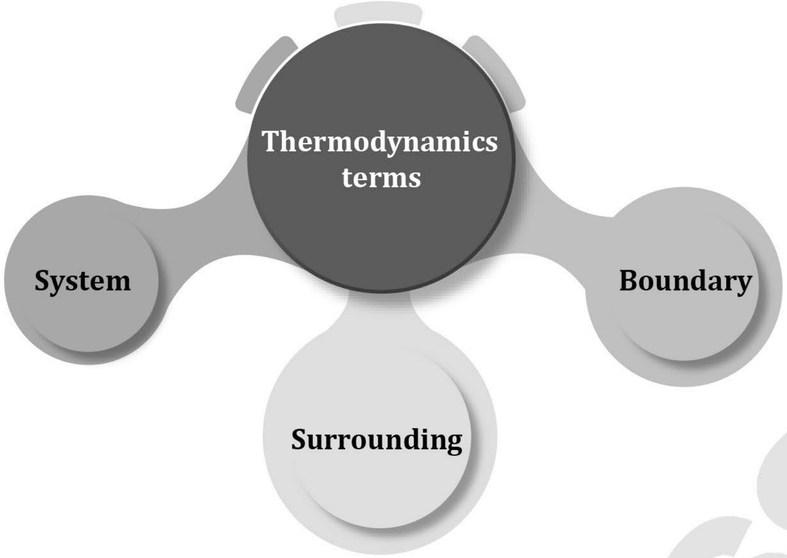
Limitations of thermodynamics :

(i) Thermodynamics deals with the properties like temperature, pressure, volume, etc. of matter in bulk but doesn't tell us anything about the individual properties of atoms or molecules.

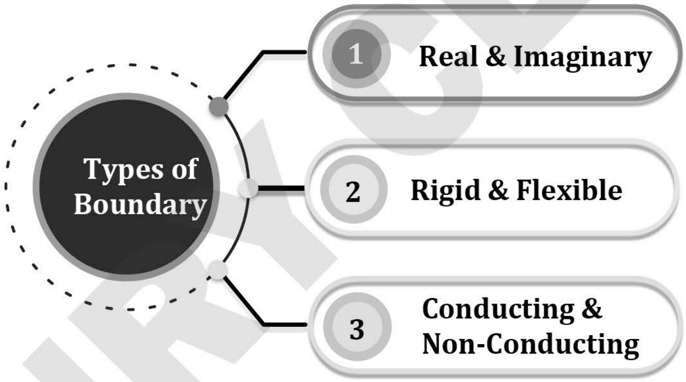
or

Thermodynamics deals with **macroscopic system** but not with **microscopic system.**

(ii) It tells us whether a given chemical reaction will take place or not under the given set of conditions but doesn't tell us anything about the **rate of reaction.**



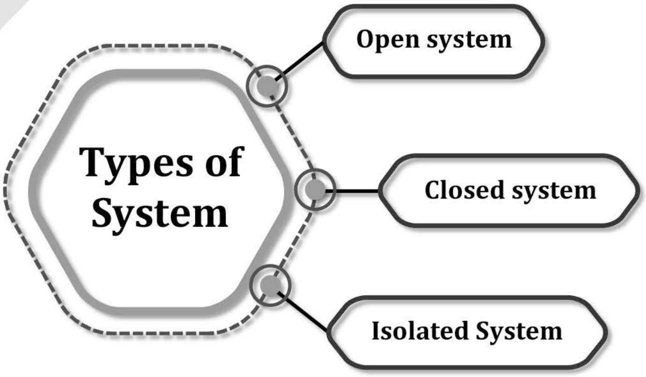
- **System :** A system is defined as a specific part of universe or specified portion of the matter which is under experimental investigation
- **Surrounding :** The rest part of the universe excluding the system is called surrounding.
  Universe = System + Surrounding
- **Boundary :** Anything which separates system and surrounding is called boundary.



For example :

A reaction is carried out in a beaker. The contents of beaker constitute the system, beaker serves as boundary and anything which is outside the beaker is called surrounding.

Types of System :



Open system : This type of system can exchange energy as well as matter with the surrounding. The boundary is neither sealed nor insulated. Total mass will not remain constant.

Eg.1 Coffee in open glass, Hot water in open glass.

Eg.2 All living systems e.g: human being, plants, animals.

Eg.3 Classroom, earth.

Closed system : This type of system can exchange energy, (in the form of heat, work or radiations) but not matter with its surroundings. The boundary is sealed but not insulated. Amount of the system will remain constant.

Eg.1 Coffee in closed vessel, Hot water in closed vessel.

Eg.2 Glowing bulb, tube light.

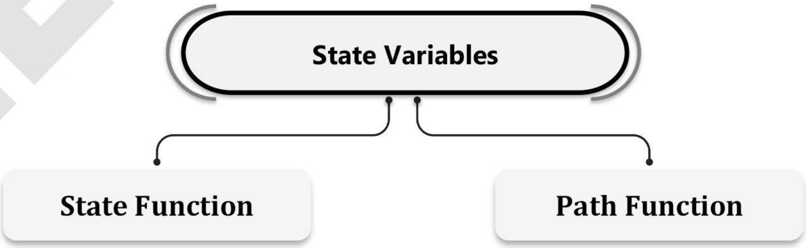
Eg.3 A satellite in orbit.

Isolated system : This type of system are perfectly insulated systems and cannot interact in any way with its surrounding i.e. neither matter nor energy can be exchanged with the surrounding. The boundary is sealed and insulated. Universe can be considered as an isolated system.

Eg.1 Coffee in thermos flask.

State of the System :

- Properties which define state of any system are called its state variables or thermodynamic variables or thermodynamic quantities.



- The state of the system is defined by its measurable properties like temperature, pressure, volume etc.
- If any of these properties change, state of the system is said to be changed.

State Function :

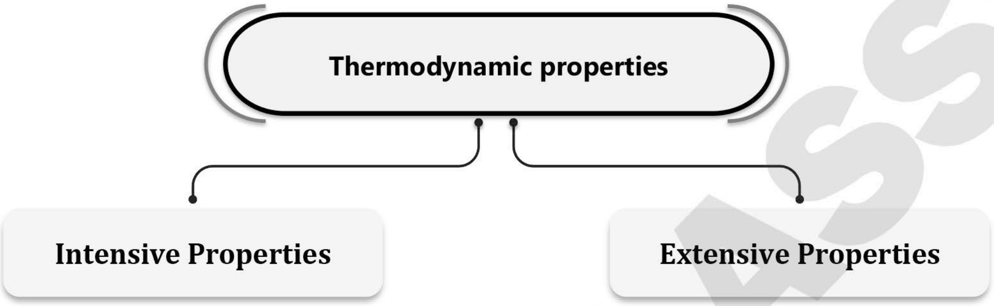
- Those state variables which depend only upon state of the system but doesn't depend upon the path or mechanism followed by the system to achieve final state are called state function.
- State functions are denoted by capital letters.

  Ex. E, H, S, G, T, P, V etc.

Path function :

- Properties of the system which depend upon the initial and final state of the system as well as the path or mechanism followed by the system to achieve final state are called path function.
- Path functions are denoted by small letters.

  Eg. Work done (w), heat (q)



(i) **Intensive properties** : The properties of the system which are independent of matter (size and mass) present in system are called intensive properties.

(ii) **Extensive properties** : The properties of the system which are dependent on matter (size and mass) present in system are called extensive properties

Extensive Properties	Intensive Properties
Volume (V)	Molar volume (V_m)
Number of moles (n)	Density (d)
Mass (M)	Gibb's energy per mole (G_m)
Gibb's Energy (G)	Specific heat
Entropy (S)	Pressure (P)
Enthalpy (H)	Temperature (T)
Internal energy (E or U)	All concentration terms (M, N)
Heat capacity (C)	Boiling point, freezing point (T_b, T_f)
Force (F)	Cell potential (E_{cell})
Surface Area (A)	Specific conductance (k)
	Refractive index
	Surface tension, Viscosity
	pH value
	Vapour pressure

Special Points

(i) The ratio of two extensive properties indicates the intensive property

Eg. $d = \frac{\text{mass}}{\text{volume}}$

(ii) An extensive property can be converted into intensive property when it is defined for unit amount of the substance.

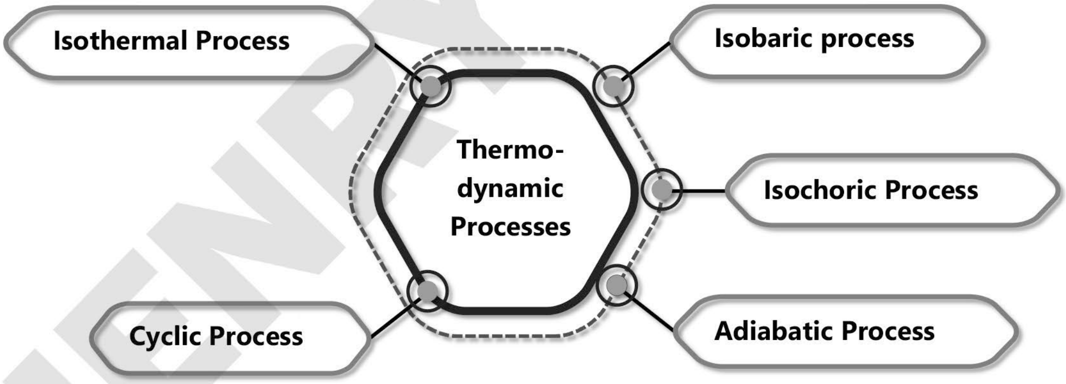
Eg. Mass per unit volume = density; $\left(d = \frac{m}{V}\right)$

(iii) Intensive properties of a substance are non-additive in nature while extensive properties are additive in nature.

Vessel	$\boxed{H_2O}$ A	$\boxed{H_2O}$ B	On adding	
Mass	m_1	m_2	$m_1 + m_2$ (Total mass)	Extensive
Moles	n_1	n_2	$n_1 + n_2$ (Total moles)	
Volume	V_1	V_2	$V_1 + V_2$ (Total volume)	
Density	d	d	Remains same (d)	Intensive
Boiling point	T	T	Remains same (T)	

Types of Thermodynamic Processes :

When a system changes from one state to another, the operation is called a thermodynamic process. Thermodynamic processes may be in form of expansion or compression.



(a) Isothermal Process (n, T = constant)

Isothermal processes are those processes in which

(a) Temperature of system during entire process remains constant i.e. (dT = 0)

(b) Heat is exchanged with surroundings

(c) Volume and pressure are variable

- For ideal gas in Isothermal process $\Delta E = 0$ and $\Delta H = 0$
- All phase transitions are isothermal process but $\Delta E \neq 0$ and $\Delta H \neq 0$

(b) Isobaric Process (n, P=constant) :

Isobaric processes are those processes in which

(a) Pressure of system during entire process remains constant i.e. $dP = 0$

(b) Volume and temperature are variable.

(c) Process in open system is isobaric in nature.

(c) Isochoric Process (n, V = constant) :

Isochoric processes are those processes in which

(a) Volume remains constant i.e. $dV = 0$

(b) Pressure and temperature are variable

(c) Work, $w = -P\Delta V$, $\because \Delta V = 0$, $\therefore w = 0$ (Zero)

(d) Process in closed system is isochoric in nature.

(d) Adiabatic Process (n = constant, q = 0)

Adiabatic processes are those processes in which

(a) No exchange of heat between system and surrounding takes place during entire process i.e. $q = 0$

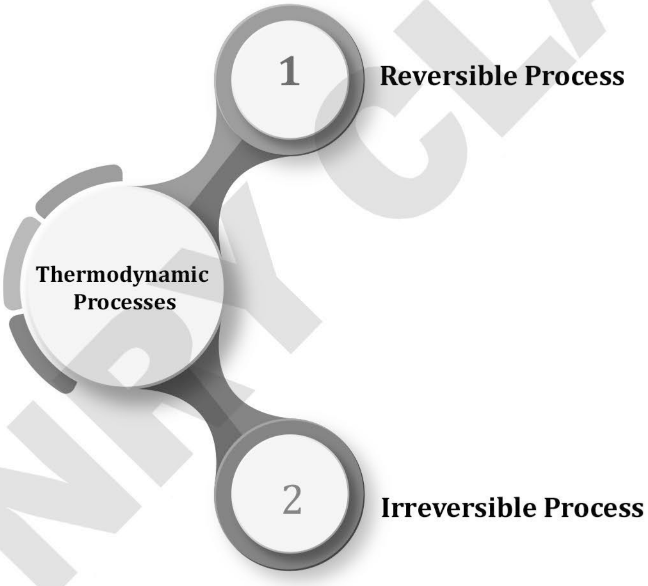
(b) The temperature, pressure, volume of the system varies.

(c) The system is thermally insulated by keeping the system in an insulated container.

(e) Cyclic Process :

When a system undergoes a number of different processes and finally returns to its initial state, it is termed as cyclic process.

In cyclic process change in all state function will be zero. i.e. $\Delta E = 0$, $\Delta H = 0$, $\Delta P = 0$, $\Delta T = 0$



Reversible Process (quasi-static) :

(1) Process in which all changes occuring at any part of the system are exactly reversed when small changes in variables are carried out in opposite direction.

(2) Driving force should be infinitesimally greater than opposing force.

(3) Process takes place in infinitesimal small steps or in many steps and takes infinite time to complete the process.

(4) It is an ideal process.

(5) Work obtained in expansion is maximum.

(6) System is in virtual equilibrium at any state.

(7) $P_{ext} = P_{int} \pm dP$; P_{ext} is variable.

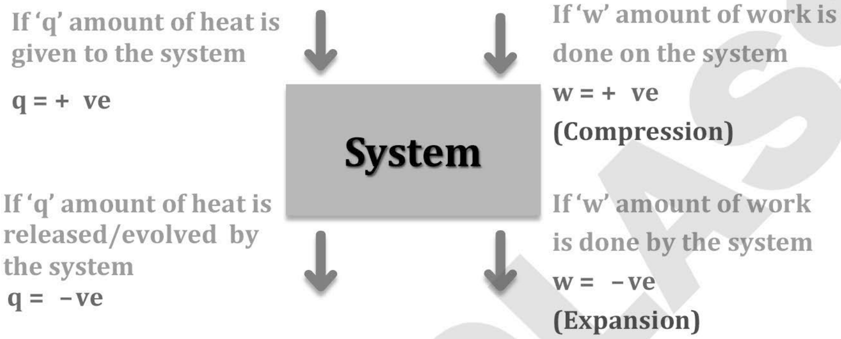
Irreversible Process :

(1) Process in which direction of change cannot be reversed by small changes in variables.
(2) Driving force is much greater than opposing force.
(3) It takes finite time and finite/usually single step.
(4) Process takes place in short time
(5) All natural processes are irreversible
(6) System is in equilibrium only at initial and final state
(7) $P_{ext} = P_{int} \pm \Delta P$; P_{ext} is constant.

Sign Conventions

The work (w) is positive, when work is done on the system and w is negative, when the work is done by the system. The heat (q) is positive, when heat is transferred from surroundings to the system and q is negative when heat is transferred from system to the surroundings.

Sign convention

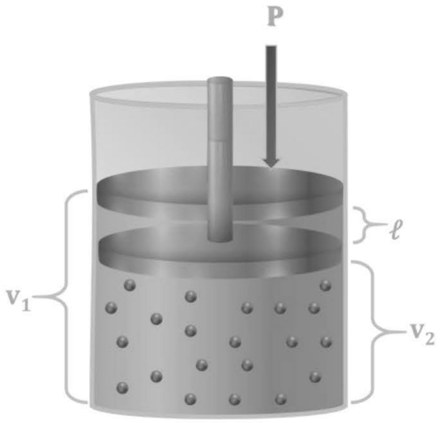


Work and Heat :

Work : Product of force and displacement is known as work.

work (w) = force (F) × displacement (ℓ)

Consider a gas enclosed in a cylinder fitted with a frictionless piston.
Suppose area of cross section of cylinder = A and pressure on the piston = P
Initial volume of the gas = V_1 and final volume of the gas = V_2
(By expansion) displacement of piston = ℓ



work done by the gas (in expansion) = w = F.ℓ

$\because P = \frac{F}{A}$ $\therefore F = P \times A$

$w = P \times A \times \ell$ (change in volume = $A \times \ell = V_2 - V_1$)

$w = P \times (V_2 - V_1)$
$w = P\Delta V$ (According to Physics)
In general
$\boxed{w = -P_{external}\,\Delta V}$ (According to Chemistry)

Units of heat & work :

Calorie: It is defined as the quantity of heat required to raise the temperature of 1 g of water by 1°C (14.5 to 15.5°C)
1 Cal = 4.184 J $\simeq$ 4.2 J
1 L-atm = 101.3 J = 24.206 Cal = 101.3×10^7 erg
$\boxed{1\ \text{L} - \text{atm} > 1\ \text{Cal} > 1\ \text{J} > 1\ \text{erg}}$

Golden Key Points

- Molar properties like H_m, G_m, S_m, U_m are intensive properties.
- In cyclic process change in all state function will be equal to zero.
  $\Delta E = 0$; $\Delta H = 0$, $\Delta P = 0$, $\Delta T = 0$ etc.
- For ideal gases $\Delta E = 0$ (For isothermal process)
- All natural process are irreversible in nature.

Illustration 1:

Find the work in each case :

(a) When one mol of ideal gas in 10 litre container at 1 atm is allowed to enter a vacuum bulb of capacity 100 litre.

(b) When 1 mol of gas expands from 1 litre to 5 litre against constant atmospheric pressure.

Solution:

(a) $W = -P\Delta V$

but since gas enters the vacuum bulb and pressure in vacuum is zero. This type of expansion is called **free expansion** and work is zero.

Note :- Work in free expansion is always zero.

(b) $W = -P\Delta V = -1(5 - 1) = -4$ L-atm.

Illustration 2:

A 5 litre cylinder contained 10 mol of oxygen gas at 27°C. Due to sudden leakage through the hole, all the gas escaped into the atmosphere and the cylinder got empty. If the atmosphere pressure is 1.0 atm. Find work (in L atm) ($R = 0.083$ L atm mol^{-1} K^{-1})

Solution:

$V_{initial} = 5$ L

$T = 27°C = 27 + 273 = 300$ K

$$V_{final} = \frac{nRT}{P} = \frac{10 \times 0.083 \times 300}{1} = 249 \text{ L}$$

$\Delta V = V_{final} - V_{initial}$

$= 249 - 5 = 244$ L

$W_{exp} = -P\Delta V$

$= -1 \times 244$ L-atm.

$= -244$ L-atm.

Internal Energy (E/U) :

Internal energy of a system is defined as the sum of different energies associated with its atoms and molecules like Potential energy, Kinetic energy (due to translatory, rotatory and vibratory motion), electronic energy, nuclear energy etc.

$E = E_{PE} + E_T + E_R + E_V + E_e + E_N$

(i) Internal energy is an **extensive property**.

(ii) We can **never find out the absolute value** of internal energy (E) of system.

We can only calculate the change in internal energy of the system (ΔE) by using an instrument which is called as Bomb calorimeter. In Bomb calorimeter reactions are carried out at constant volume.

(iii) Internal energy is a **state function**.

$\Delta E = E_f - E_i$

(In reaction) $\Delta E = E_P - E_R$

ΔE is + ve if $E_f > E_i$

ΔE is – ve if $E_f < E_i$

Laws of Thermodynamics :

General Point :

Laws of thermodynamics are based on human experiences and there is no formal proof for them.

First Law of Thermodynamics (FLOT) :

- This law is based on law of conservation of energy and was given by **Robert Mayer and Helmholtz.**
- Energy can neither be created nor destroyed but can be transformed from one form to another.
- The total energy of the universe is always constant. i.e. total energy of an isolated system is always conserved.
- The mathematical form of first law of thermodynamics can be expressed as follows

  $\Delta E = q + w$: where q, w are path function and E is state function.

  Here q is the energy given to the system and w is the work done on the system; ΔE is change in internal energy.

Illustration 3:

1g of water changes from liquid to vapour phase at constant pressure of 1 atmosphere, the volume increases from 1 mL to 1671 mL. The heat of vaporisation at this pressure is 540 Cal g^{-1} Find the increase in internal energy of water. (1 L atm = 101 J)

Solution:

Work done

$w = -P\Delta V = -P(V_2 - V_1)$

$= -1(1671 - 1) \times \frac{1}{1000} = \frac{-1670}{1000}$ L – atm

$= \frac{-1670}{1000} \times 101 \text{ J} = -168.67 \text{ J}$

given that q = 540 Cal = 540 × 4.2 J = 2268 J

$\therefore \Delta E = q + w = 2268 - 168.67 = 2099.33$ J

Illustration 4:

A gas occupies 2 L at STP. It is provided 300 J heat so that its volume becomes 2.5 L at 1 atm. Calculate change in its internal energy.

Solution:

$w = -P\Delta V = -1 \times (2.5 - 2) = -0.5$ L-atm or $w = -0.5 \times 101.3 = -50.65$ J.

$\Delta E = q + w = 300 + (-50.65)$

$\Delta E = 249.35$ J

Illustration 5:

A sample of gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2L to 12L. During the process, it absorbs 600 J of heat from the surroundings. Calculate the change in internal energy of the system.

Solution:

During the process,

$q = 600$ J, $\Delta V = 12 - 2 = 10$ L, $P = 1$ atm

$w = -P\Delta V$

$= -1 \times 10 \quad = -10$ L atm

Now, 1 L atm = 101.3 J

$\therefore w = -10 \times 101.3 = -1013$ J

According to first law of thermodynamics,

$\Delta E = q + w = 600 - 1013 = -413$ J

Illustration 6:

Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half of its volume by a constant external pressure of 4 atm. Calculate q, w & ΔE. ($R = 0.082$ L atm mol^{-1} K^{-1})

Solution:

$w = -P_{ext}\Delta V = -P_{ext}(V_f - V_i)$

$V_i = \dfrac{nRT}{P}$

$n = 2$ mol and $R = 0.082$ atm L mol^{-1} K^{-1},

$T = 273 + 27 = 300$ K, $P = 2$ atm

$V_i = \dfrac{2\times0.082\times300}{2} = 24.6$ L and $V_f = \dfrac{V_i}{2} = \dfrac{24.6}{2} = 12.3$ L

$w = -4$ atm × (12.3 – 24.6) L

$= 49.2$ L atm

$= 49.2 \times 101.3$ J = 4984 J.

Since, it is isothermal compression, $\Delta E = 0$

Now, $\Delta E = q + w$

$0 = q + 4984$ J or $q = -4984$ J

Illustration 7:

A system is provided with 100 J of heat. Work done on the system is 20 J. What is the change in internal energy ?

Solution:

q = 100 J and w = +20 J

$\Delta E = q + w$

= 100 + 20 J = 120 J

Illustration 8:

An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T, while the other portion is a perfect vacuum. If a hole is opened between the two portions, Calculate the –

(i) Change in internal energy of the gas

(ii) Change in temperature of the gas

Solution:

For insulated system, q = 0

The gas is allowed to expand against vacuum, the process of free expansion and thus

$w = -P\Delta V = 0$ (for vacuum = $P_{ext} = 0$)

Thus from first law of thermodynamics, $\Delta E = q + w$ or $\Delta E = 0$

i.e. internal energy change is zero or internal energy of gas remains constant during free expansion.

Also $E \propto T$ and thus temperature of the gas will also remain constant.

Conclusions from the First Law of Thermodynamics :

(a) During isothermal process of an ideal gas :

During an isothermal process the temperature of the system remains constant and hence

$\Delta E = 0$

Therefore

FLOT : $\Delta E = q + w$

$\therefore +q = -w$ or $-q = +w$

In isothermal process –

(I) Heat absorbed by the system is equal to work done by the system.

OR

(II) Heat evolved by the system is equal to work done on the system.

(b) During isochoric process :

At constant volume $V_1 = V_2$ i.e. $\Delta V = 0$

Hence $W = -P\Delta V = 0$ .... No work done at constant volume therefore,

FLOT: $\Delta E = q + w$

$\Rightarrow \Delta E = q_v$

(i) In isochoric process

- At constant volume, heat absorbed by the system is equal to increase in internal energy of the system.

OR

- At constant volume, heat evolved by the system is equal to decrease in internal energy of the system.

(ii) Heat at constant volume (q_v) = ΔE

(iii) **In isochoric process heat is independent of path.**

(c) During adiabatic process :

During adiabatic process the system acts as an isolated system and hence **q = 0** in such cases. Therefore

FLOT : $\Delta E = q + w \quad \because q = 0 \quad \boxed{\Delta E = w}$

(i) Work done on the system is equal to increase in internal energy of the system i.e., when a gas is compressed adiabatically its internal energy increases.

OR

Work done by the system is equal to decrease in internal energy of the system, i.e., when a gas is expanded adiabatically its internal energy decreases.

(ii) **In adiabatic process work is independent of path.**

(d) During Cyclic Process :

$\Delta E = 0$ FLOT ; $\Delta E = q + w \quad \Rightarrow q = -w$

In cyclic process.

(I) Work done by the system is equal to heat absorbed by the system.

OR

(II) Work done on the system is equal to heat evolved by the system.

(e) During Isobaric process :

P is constant

FLOT :
$$\Delta E = q + w$$
$$\Delta E = q + (-P\Delta V)$$
$$q_p = \Delta E + P\Delta V$$
$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$
$$q_p = (E_2 + PV_2) - (E_1 + PV_1)$$
$\because$ Enthalpy $H = E + PV$

$\therefore \quad q_p = H_2 - H_1 \qquad \boxed{q_p = \Delta H}$

(i) **In Isobaric process :**

- At constant pressure, heat absorbed by the system is equal to increase in enthalpy of the system.

OR

- At constant pressure, heat evolved by the system is equal to decrease in enthalpy of the system.

(ii) Heat at constant pressure (q_p) = ΔH

(iii) **In isobaric process heat is independent of path.**

Enthalpy (H) :

Mathematically it is heat contained in the system measured at constant pressure.

The sum of internal energy and pressure volume (PV) energy is known as enthalpy.

$$\Delta H = \Delta E + \Delta(PV)$$

- It is impossible to determine absolute value of enthalpy, so, we determine change in enthalpy (ΔH).

  $\Delta H = H_{final} - H_{initial}$
- Enthalpy is an extensive property because E and V are extensive properties.
- It is a state function because E, P and V are state functions.

  $\because \quad H = E + PV$

  $\therefore \quad \Delta H = \Delta E + \Delta(PV)$ ...(i)

  (when P, V and T are variables)

  At constant pressure : $\Delta H = \Delta E + P.\Delta V$ ...(ii)

  At constant volume : $\Delta H = \Delta E + V.\Delta P$ ...(iii)

  For chemical reactions at constant temperature and pressure

  $\therefore P.\Delta V = \Delta n_g RT$

  So from equation (i) $\Delta H = \Delta E + \Delta n_g RT$ ...(iv)

  where $\Delta H = q_p$; at constant P ; $\Delta E = q_v$; at constant V

  So equation (iv) can be also written as $q_p = q_v + \Delta n_g RT$ ...(v)

Golden Key Points

- If, $\Delta n_g = 0 \rightarrow \boxed{\Delta H = \Delta E}$ eg. $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- If, $\Delta n_g > 0 \rightarrow \boxed{\Delta H > \Delta E}$ eg. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- If, $\Delta n_g < 0 \rightarrow \boxed{\Delta H < \Delta E}$ eg. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

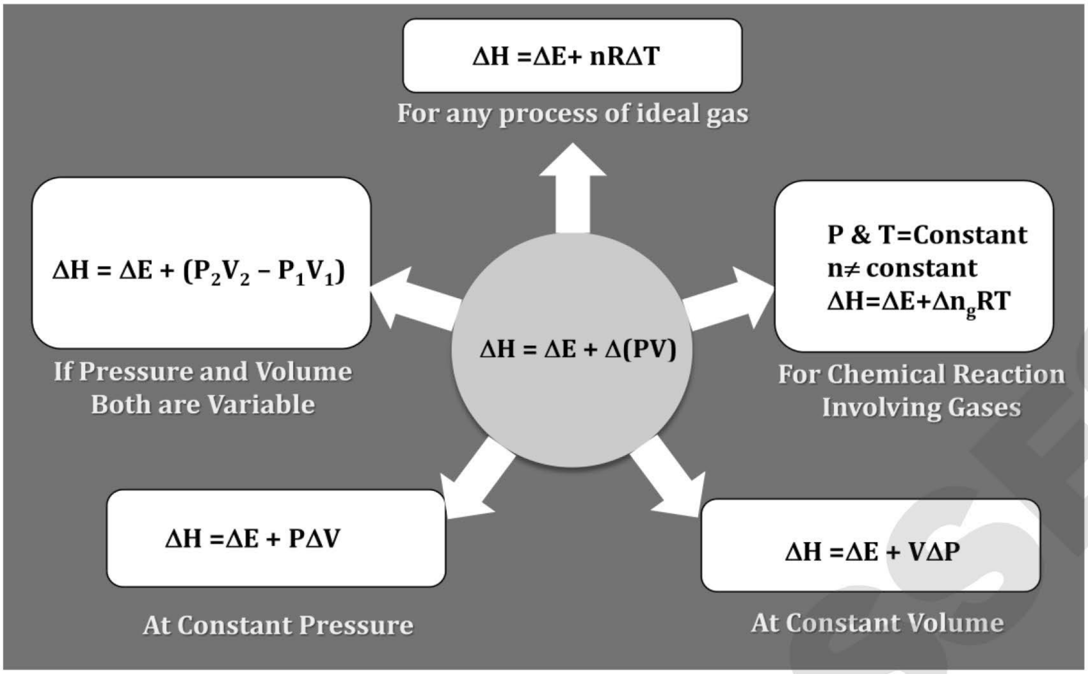


Illustration 9:

The heat of reaction for $C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(\ell)$ at constant volume is – 1228.2 kCal at 25°C. Calculate the heat of reaction at constant pressure and at 25°C.

Solution:

$\Delta n_g = [10] - [12] = -2$

$\Delta H = \Delta E + \Delta n_g RT$

$= -1228.2 \times 10^3 + (-2)(2) \times 298$

$= -1229392$ Cal

$\Delta H = -1229.392$ kCal

Illustration 10:

For the reaction at 25°C

$$NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)\ ;\ \Delta H^\circ = 11.04 \text{ kCal.}$$

Calculate ΔE° of the reaction at the given temperature.

Solution:

$\Delta H^\circ = \Delta E^\circ + \Delta n_g RT$

$\Delta n_g = 2 - 1 = 1$ mol

$\Delta E^\circ = \Delta H^\circ - \Delta n_g RT$

$= 11.04 \text{ Kcal} - 1 \text{ mol} \times \frac{2}{1000} \text{ kCal mol}^{-1}\text{K}^{-1} \times 298\text{K}$

$= 11.04 - 0.596 = 10.44$ kCal

Illustration 11:

At 27°C the internal energy change of reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ is 2Cal. What is the enthalpy change of this reaction ?

Solution:

$\Delta H = \Delta E + \Delta n_g RT$

$\Delta H = \Delta E + 0 \times RT$

$\Delta H = \Delta E$

$\Delta H = 2\text{Cal}$

Illustration 12:

The heat of combustion of gaseous methane (CH_4) at constant volume is measured in bomb calorimeter at 298K is found to be –885.4 kJ mol⁻¹. Find the value of enthalpy change at the same temperature.

Solution:

Combustion of methane gives $CO_2(g)$ and $H_2O(\ell)$ as

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(\ell)$

$\Delta E = -885.4 \text{ kJ mol}^{-1} = -885400 \text{ J mol}^{-1}$

$\Delta n_g = 1 - (1 + 2) = -2 \text{ mol}$

$T = 298\text{K}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Now, $\Delta H = \Delta E + \Delta n_g RT$

$= -885400 + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298\text{K})$

$= -885400 - 4955$

$= -890355 = -890.355 \text{ kJ}$

Illustration 13:

The enthalpy change (ΔH) for the reaction : $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is – 92.38 kJ at 298 K. What is ΔE at 298 K ?

Solution:

ΔH and ΔE are related as $\Delta H = \Delta E + \Delta n_g RT$

for the reaction, $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

$\Delta n_g = 2 - (1 + 3) = -2 \text{ mol}, T = 298 \text{ K}$

$\Delta H = -92.38 \text{ kJ} = -92380 \text{ J}, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

$-92380 = \Delta E + (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$

$-92380 = \Delta E - 4955$

$\Delta E = -92380 + 4955$

$= -87425 \text{ J} = -87.425 \text{ kJ}.$

Illustration 14:

The enthalpy change for the reaction $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ at 1000K is 176 kJ mol⁻¹. Calculate the change in internal energy.

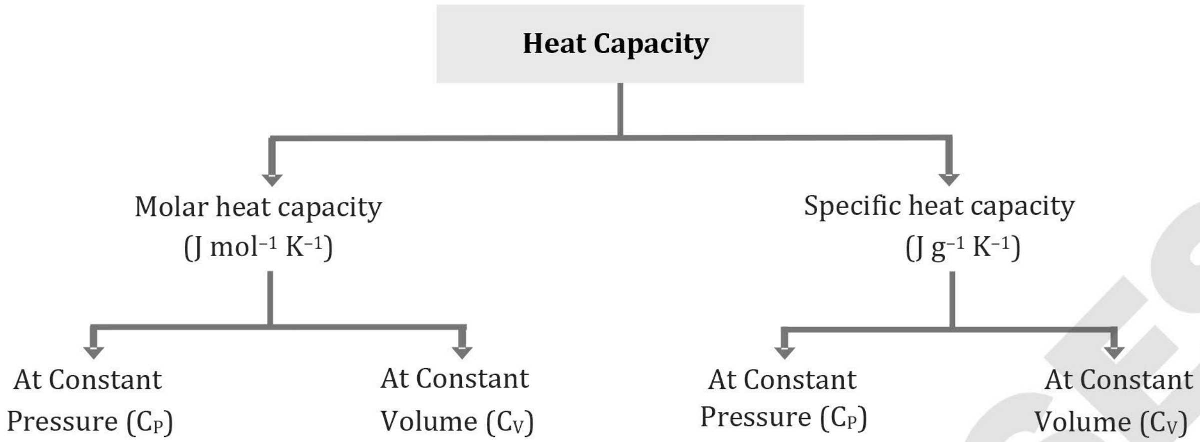
Solution:

$\Delta H = \Delta E + \Delta n_g RT$

$176 = \Delta E + (+1) \times 8{\cdot}314 \times 10^{-3} \times 1000$

$\Delta E = 167{\cdot}686 \text{ kJ}$

Heat Capacity / Molar Heat Capacity / Specific Heat Capacity :



(i) **Heat capacity (C) :** Amount of heat required to raise the temperature of given amount of a substance by 1°C or 1K is called heat capacity.

$$\text{Heat capacity} = \frac{\text{Heat required}}{\text{rise in temp.}}$$

$$\boxed{C = \frac{dq}{dT}}$$

Units :- JK^{-1}, Cal K^{-1}, J $°C^{-1}$, Cal $°C^{-1}$

- Heat capacity is extensive property.

(ii) **Molar heat capacity (C_m) :** Amount of heat required to raise the temperature of 1 mole of substance by 1°C or 1 K is called as molar heat capacity.

$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{mole of substance}} \Rightarrow \boxed{C_m = \frac{C}{n}}$$

Units :- $\text{J mol}^{-1}\,\text{K}^{-1}$, $\text{Cal mol}^{-1}\,\text{K}^{-1}$, $\text{J mol}^{-1}\,{}^\circ\text{C}^{-1}$, $\text{Cal mol}^{-1}\,{}^\circ\text{C}^{-1}$

- Molar heat capacity is an intensive property.

(iii) **Specific heat capacity (c) :** Amount of heat required to raise the temperature of 1 g of substance by 1°C or 1K is called as specific heat capacity.

$$\boxed{c = \frac{C_m}{\text{molecular weight}}}$$

Units :- $\text{J g}^{-1}\,\text{K}^{-1}$, $\text{Cal g}^{-1}\,\text{K}^{-1}$, $\text{J g}^{-1}\,{}^\circ\text{C}^{-1}$, $\text{Cal g}^{-1}\,{}^\circ\text{C}^{-1}$

- Specific heat capacity is an intensive property.
- If heat is suppplied at constant pressure, then $C_P = \left(\frac{dq}{dT}\right)_P = \frac{dH}{dT}$ ...(i)
- If heat is supplied at constant volume, then $C_V = \left(\frac{dq}{dT}\right)_V = \frac{dE}{dT}$ ...(ii)

From equation (i) and (ii) :

From equation (i)	Unit	From equation (ii)
$\Delta H = C_P dT$ [Here C_P is heat capacity at constant P]	JK^{-1}	$\Delta E = C_V dT$ [Here C_V is heat capacity at constant V]
For n moles $\Delta H = nC_{P,m}dT$ [Here $C_{p,m}$ is molar heat capacity at constant p]	$\text{J mol}^{-1}\text{K}^{-1}$	$\Delta E = nC_{V,m}dT$ [Here $C_{V,m}$ is molar heat capacity at constant V]
For m gram $\Delta H = mc_p dT$ [Here C_p is gram specific heat (specific heat capacity) at constant P]	$\text{J g}^{-1}\,\text{K}^{-1}$	$\Delta E = mC_V dT$ [Here C_v is gram specific heat (specific heat capacity) at constant V]

Relation between C_P and C_V for 1 mole of an ideal gas :

$\because$ $H = E + PV$

for ideal gas,

$PV = nRT$

$PV = RT$ for 1 mole

$\therefore$ $H = E + RT$ differentiate w.r.t. temperature

$$\left(\frac{dH}{dT}\right) = \left(\frac{dE}{dT}\right) + R$$

$$C_{P,m} = C_{V,m} + R$$

(i) $\boxed{C_{P,m} - C_{V,m} = R}$ Mayer's formula

(ii) $\boxed{\frac{C_P}{C_V} = \gamma}$, γ = Poisson's ratio

Work Done in Different Process :

(a) Work done in reversible isothermal process :

$P_{external}$ = Variable

For reversible process

$P_{ext} = P_{gas} \pm dP$

$\because \quad w_{rev.} = -\int_{v_1}^{v_2} P_{ext.}\, dV$

$$w_{rev.} = -\int_{v_1}^{v_2} (P_{gas} \pm dP).dV$$

Both dP and dV are very small so, (dP.dV) is negligible.

$$w_{rev.} = -\int_{v_1}^{v_2} P_{gas}.dV$$

$$w_{rev.} = -\int_{v_1}^{v_2} \frac{nRT}{V}.dV$$

$$w_{rev.} = -nRT\int_{v_1}^{v_2} \frac{dV}{V}$$

$$w_{rev.} = -nRT\ell n\left(\frac{V_2}{V_1}\right)$$

or, $$w_{rev.} = -2.303\ nRT\ \log_{10}\left(\frac{V_2}{V_1}\right) \qquad ...(i)$$

according to Boyle's law at constant temperature $P \propto \frac{1}{V}$ or PV = constant

$\therefore \quad P_1V_1 = P_2V_2 \quad \Rightarrow \quad \frac{V_2}{V_1} = \frac{P_1}{P_2}$

$$w_{rev.} = -2.303\ nRT\ \log_{10}\left(\frac{P_1}{P_2}\right) \qquad ...(ii)$$

(b) Work done in reversible adiabatic process :

In adiabatic process q = 0

FLOT : $\Delta E = q + w$

$\Rightarrow w = \Delta E \Rightarrow w = nC_{V,m}\Delta T$

$$w = nC_{V,m}(T_2 - T_1) \qquad ...(i)$$

$\because \quad C_{P,m} - C_{V,m} = R$

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V} \left(\because \gamma = \frac{C_P}{C_V}\right) \Rightarrow C_V = \frac{R}{\gamma - 1} \qquad ...(ii)$$

From equation (i) and (ii) $w = \frac{nR}{\gamma - 1}(T_2 - T_1) = w = \frac{P_2V_2 - P_1V_1}{(\gamma - 1)}$

State equations of reversible adiabatic process are :

PV^{γ} = constant

$TV^{\gamma - 1}$ = constant

$T^{\gamma}P^{1 - \gamma}$ = constant

Golden Key Points

- Work in rigid vessel is zero because volume remains constant.
- Work during free expansion of an ideal gas in vacuum is zero, because P_{ext} is zero.
- Work in a chemical reaction $w = -P\Delta V = -\Delta n_g.RT$

Illustration 15:

5 moles of oxygen are heated at constant volume from 10°C to 20°C. What will be the change in the internal energy of gas? The molar heat capacity of oxygen at constant pressure,

$C_p = 7.03 \dfrac{\text{Cal}}{\text{mol K}}$ and R=2 Cal $\text{mol}^{-1}\,\text{K}^{-1}$

Solution:

We know mayer's relation is $C_{P,m} - C_{v,m} = R$

$C_{v,m} = C_{p,m} - R = 7.03 - 2 = 5.03$ Cal $\text{mol}^{-1}\,\text{K}^{-1}$

As we know $\Delta E = nC_{v,m}dT = 5 \times 5.03 \times 10 = 251.5$ Cal

Illustration 16:

At 27°C, one mole of an ideal gas compressed isothermally and reversibly from a pressure of 2 atm to 10 atm. Calculate ΔE and q in calorie.

Solution:

For isothermal process $\Delta E = 0$ and $w = -2.303\ nRT \log_{10}\left(\dfrac{P_1}{P_2}\right)$

$w = -2.303 \times 1 \times 2 \times 300 \times \log\left(\dfrac{2}{10}\right)$

$w = +2.303 \times 600 \times \log 5$

$w = +2.303 \times 600 \times 0.699$

$w = +965.87$ Cal

For isothermal process

$\because\ w = -q$

$\therefore\ q = -965.87$ Cal

Illustration 17:

A gas expands from 3dm³ to 5 dm³ against a constant pressure of 3 atm. The work done during expansion is used to heat 10 mol of water of temperature 290 K. Calculate final temperature of water (if specific heat of water is 4.184 $\text{Jg}^{-1}\text{K}^{-1}$)

Solution:

Since work is done against constant P and thus, irreversible

$\Delta V = 5 - 3 = 2\text{dm}^3 = 2$ L, P = 3 atm

$w = -P\Delta V = -3 \times 2$ L atm $= -6 \times 101.3$ J $= -607.8$ Joule

Now this work is used up in heating water

$w = n \times C \times \Delta T$

$607.8 = 10 \times (4.184 \times 18) \times \Delta T$

$\Delta T = 0.81 = T_2 - T_1$

$\therefore$ Final temperature $= T_1 + \Delta T = 290 + 0.81 = 290.81$ K

Illustration 18:

A sample of 3 mol of an ideal gas at 200K and 2 atm is compressed reversibly and adiabatically until the temperature reaches 250K, given that molar heat capacity is 27.5 Jk^{-1} mol^{-1} at constant volume, calculate w.

Solution:

$C_{v,m} = 27.5$ Jk^{-1}mol^{-1}

During reversible adiabatic process

$w = nC_{V,m}(T_2 - T_1) = 3 \times 27.5 \times 50 = 4125$ Joule

Illustration 19:

10 moles of an ideal gas at 27°C and 10 atm. pressure occupying a volume of 24.6 L undergoes the following changes.

(i) Isothermal & reversible expansion to 246 L

(ii) Isothermal and irreversible expansion to 246 L.

(iii) Isochoric heating to 177°C.

Calculate the work in each transformation in kJ.

Solution:

(i) Work in isothermal reversible process

$$w = -2.303 \times nRT \log\left(\frac{V_2}{V_1}\right)$$

$$= -2.303 \times 10 \times 8.31 \times 300 \times \log\left(\frac{246}{24.6}\right)$$

$$= -57413.79 \text{ J} = -57.41 \text{ kJ}$$

(ii) Work in isothermal irreversible expansion process

$w = -P(V_2 - V_1) = -10(246 - 24.6) = -2214$ L-atm

$= -2214 \times 101.3$ J $= -224.3$ kJ

(iii) Work in isochoric change

Since, $\Delta V = 0$ $\therefore w = 0$

Illustration 20:

Find the work, when 2 mol of a gas expands isothermally from 5dm^3 to 40dm^3 against a constant external pressure of 2 atm at 298K. Also calculate w_{rev} for the change.

Solution:

(i) $w = -P\Delta V$

$w = -2 \times (40 - 5)$

$w = -70$ L atm $= -70 \times 101.3$ J

$w = -7091$ J

(ii) $w = -2.303\, nRT \log\left(\frac{V_2}{V_1}\right)$

$$w = -2.303 \times 2 \times 8.314 \times 298 \log\left(\frac{40}{5}\right)$$

$$w = -10.3 \times 10^3 \text{ J}$$

Spontaneous Process and Non-Spontaneous Process

(i)
Spontaneous process

(ii)
Non-spontaneous process

(i) Spontaneous process :

- The process which has a natural tendency to occur in a particular direction either of its own or after proper initiation under the given set of conditions.
- All natural processes are ir-reversible and spontaneous processes. The natural processes take place on their own in one direction only.

(ii) Non–spontaneous process :

- The process which does not occur on its own in a particular direction i.e. a process which does not have a natural tendency to occur in a particular direction either of its own or after initiation is called as non-spontaneous process.
- Non-spontaneous process may be made to occur when energy from some external source is supplied continuously throughout the process.

Examples of spontaneous process that need no initiation :

Ex.1 Flow of water from high level to low level.
Flow of heat from hot body to cold body.
Flow of charge from high potential to low potential.
Flow of gas from high pressure to low pressure.

Ex.2 Melting of ice at 25° C
Evaporation of water at 25° C
Dissolution of common salt in water.

Ex.3 Mixing of different non reacting gases

Examples of spontaneous process that need initiation :

Ex.1 Burning of fuel (coal, petrol)

$C(s) + O_2 \rightarrow CO_2$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Ex.2 Lightning of candle

Criteria for a process to be spontaneous :

(i) Tendency to attain minimum energy or maximum stability (Energy Factor).

(ii) Tendency to attain maximum randomness (Entropy Factor)

Entropy (s) :

(i) The thermodynamic quantity, which is used to measure **degree of randomness** or **disorderness** of the system is called as entropy.

Entropy (s) $\propto$ Randomness or disorderness

(ii) More is the disorderness, higher is the entropy.

(iii) The ratio of heat absorbed by the system in isothermal and reversible manner to the temperature at which heat is absorbed is equals to the change in entropy.

$$\boxed{\Delta S = \frac{q_{rev}}{T}}$$

Where q_{rev}= heat absorbed by the system in a reversible manner at the temperature T

Unit : J K^{-1} or Cal K^{-1}

(iv) $\Delta S = S_{final} - S_{inital}$

If $S_{final} > S_{initial}$: Then ΔS = positive

If $S_{final} < S_{initial}$: Then ΔS = negative

(v) Entropy is an extensive property and state function.

Factors affecting entropy of system :

(I) If $\Delta n_g > 0$ then $\Delta S > 0$

If $\Delta n_g < 0$ then $\Delta S < 0$

(II) Physical state : $S_{solid} < S_{liquid} < S_{gas}$

(III) On increasing gaseous moles entropy increases.

(IV) On increasing temperature, S will increase.

Ex. $\underset{300\text{ K}}{Fe(s)} \rightarrow \underset{400\text{ K}}{Fe(s)}$: ΔS = positive

(V) On decreasing pressure, S increases.

Ex. $\underset{5\text{ atm}}{N_2(g)} \rightarrow \underset{2\text{ atm}}{N_2(g)}$: ΔS = positive

(VI) Mixture :

$$\left.\begin{array}{c}\text{Solid} + \text{solid}\\ \text{liquid} + \text{liquid}\\ \text{gas} + \text{gas}\end{array}\right\} S\uparrow$$

Some famous or extra ordinary examples of entropy change :

(i) Entropy of graphite > Entropy of diamond.

(ii) $NH_4Cl(s) + aq \longrightarrow NH_4^+(aq) + Cl^-(aq)$

In this process NH_4^+ and Cl^- ions are free to move in solution where as they are not free to move in solid NH_4Cl.

Hence ΔS is positive for this type of dissolution process.

(iii) On addition of HCl in the aqueous solution of Ag^+ ions entropy decreases due to precipitation of AgCl.

(iv) **On boiling of egg :** Denaturation of proteins occur. Thus entropy increases.

(v) **Stretching of rubber :** During stretching of rubber band its long flexible macromolecules get uncoiled. The uncoiled form has more specific geometry and more ordered arrangement. Thus entropy decreases.

Entropy change in a chemical reaction $\Delta S = \sum S_{Product} - \sum S_{Reactant}$

Entropy change for a process : $\Delta S = nC_V \ell n\left(\frac{T_2}{T_1}\right) + nR\,\ell n\left(\frac{V_2}{V_1}\right)$ or $\Delta S = nC_P \ell n\left(\frac{T_2}{T_1}\right) + nR\,\ell n\left(\frac{P_1}{P_2}\right)$

Case I : For an ideal gas reversible isothermal process; : $T_2 = T_1$

$$\Delta S = nR\ell n\left(\frac{V_2}{V_1}\right) = nR\,\ell n\left(\frac{P_1}{P_2}\right)$$

$$\Delta S = 2.303 nR \log\left(\frac{V_2}{V_1}\right) = 2.303 nR \log\left(\frac{P_1}{P_2}\right)$$

Case II : For an isochoric process $V_2 = V_1$

$$\Delta S = nC_V \ell n\left(\frac{T_2}{T_1}\right) \; ; \; \Delta S = 2.303\, nC_V \log\left(\frac{T_2}{T_1}\right)$$

For reversible adiabatic process : $q_{rev} = 0$, $\Delta S = \frac{q_{rev}}{T} = 0$, S = constant

Entropy remains constant so process is also known as **isoentropic process**.

Entropy change during phase transition :

(I) Entropy of fusion $[(\Delta S)_f]$:

The entropy change, when 1 mol solid changes into liquid at its melting point temperature.

solid $\rightleftharpoons$ liquid

$$(\Delta S)_f = \frac{\Delta H_{fusion}}{T}$$

(II) Entropy of vapourisation $[(\Delta S)_{vap}]$:

The entropy change, when 1 mol liquid changes into vapour at its boiling point temperature.

liquid $\rightleftharpoons$ vapour

$$(\Delta S)_{vap} = \frac{\Delta H_{vap}}{T}$$

(III) Entropy of sublimation $[(\Delta S)_{sub}]$:

The entropy change, when 1 mol solid changes into vapour at a particular temperature.

solid $\rightleftharpoons$ vapour

$$(\Delta S)_{sub} = \frac{\Delta H_{sub}}{T}$$

Total entropy change in reversible process :

In reversible process, at every step system and surroundings remain in thermal equilibrium with each other. Let a system, releases q heat to the surroundings at temperature T.

$$\Delta S_{system} = \frac{-q_{system}}{T}\ ; \qquad \Delta S_{surroundings} = \frac{+q_{system}}{T}$$

$\because \quad \Delta S_{system} = \Delta S_{system} + \Delta S_{surroundings}$

$$\Delta S_{total} = \frac{-q_{system}}{T} + \frac{q_{system}}{T} \Rightarrow \boxed{\Delta S_{total} = 0}$$

Total entropy change in irreversible process :

Let a system is at high temperature T_1 and surroundings are at low temperature T_2.

Let q amount of heat is released by the system.

$$\Delta S_{system} = \frac{-q}{T_1}, \qquad \Delta S_{surroundings} = \frac{+q}{T_2}$$

$\because \quad \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = \frac{-q}{T_1} + \frac{q}{T_2}$

$\therefore \quad \boxed{\Delta S_{total} = +ve} \quad (\because T_1 > T_2)$

Total entropy change for irreversible spontaneous process is always greater than zero.

Spontaneity of a process in terms of total entropy change :

If $\Delta S_{total} = +ve \Rightarrow$ Spontaneous process
If $\Delta S_{total} = -ve \Rightarrow$ Non spontaneous process
If $\Delta S_{total} = 0 \Rightarrow$ Process is at equilibrium

Illustration 21:

The enthalpy change for transition of liquid water to steam is 40.8 kJ mol^{-1} at 373K. Calculate ΔS for the process.

Solution:

The entropy change for the vapourization of water is given by $\Delta S = \frac{\Delta H_{vap}}{T}$

Given $\Delta H_{vap.}$ = 40.8 kJ mol^{-1} = 40.8 × 1000 J mol^{-1} and T = 373 K

$$\Delta S = \frac{40.8 \times 1000\,J\ mol^{-1}}{373K} = 109.38\ JK^{-1}\ mol^{-1}$$

Illustration 22:

Calculate the change in entropy for the fusion of 1 mol of ice. The melting point of ice is 273K and molar enthalpy of fusion of ice = 6 kJ mol^{-1}

Solution:

$$\Delta S_f = \frac{\Delta H_f}{T} = \frac{6 \times 10^3}{273} = 21.97\ JK^{-1}\ mol^{-1}$$

Illustration 23:

The enthalpy of vapourisation of liquid diethyl ether $(C_2H_5)_2O$, is 26.0 kJ mol^{-1} at its boiling point (35.0°C). Calculate ΔS for conversion of :-

(i) Liquid to vapour and

(ii) Vapour to liquid at 35°C

Solution:

(i) $\Delta S_{vap.} = \frac{\Delta H_{vap.}}{T} = \frac{26\times10^3}{308} = 84.41\ JK^{-1}mol^{-1}$

(ii) $\Delta S_{cond.} = \frac{\Delta H_{cond.}}{T} = \frac{-26\times10^3}{308} = -84.41\ JK^{-1}mol^{-1}$

Illustration 24:

Which of the following processes are accompanied by increase of entropy :

(i) Dissolution of iodine in a solvent $\{I_2(s) \longrightarrow I_2(aq.)\}$

(ii) HCl is added to $AgNO_3$ and a precipitate of AgCl is obtained.

(iii) A partition is removed to allow two gases to mix.

Solution:

Increase of entropy : (i) and (iii)

Second Law of Thermodynamics (SLOT) :

(i) It states about the direction of flow of heat

(ii) All natural processes in universe are ir-reversible process or natural processes are spontaneous process.

(iii) Due to spontaneous process entropy of universe is increasing continuously i.e. entropy of an isolated system increases.

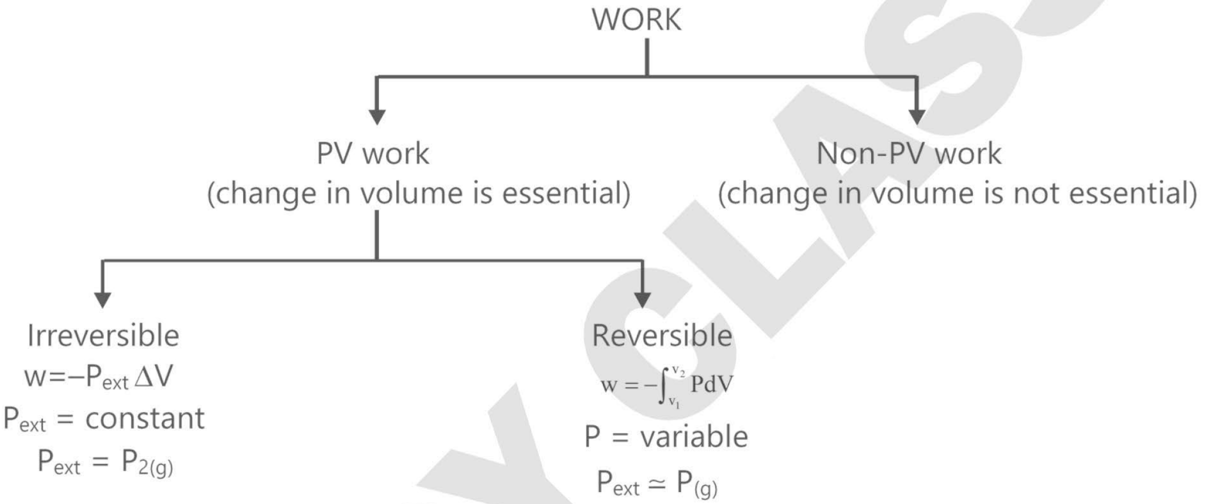
$(\Delta S)_T = +\text{ ve}$

or $(\Delta S)_T > 0$

or $(\Delta S)_{\text{system}} + (\Delta S)_{\text{surr.}} > 0$

Gibb's Energy (G or F) :

- Gibb's energy is defined at constant temperature and pressure to predict spontaneity of a process.
- Gibb's energy is a thermodynamic quantity which is used to measure the capacity of system to do useful work or Gibb's energy is that part of the total energy of system which can be converted into useful work.



Here $P_{2(g)}$ = External pressure acting from outside the piston.

$P_{(g)}$ = Pressure of gas inside the piston.

- The term Gibbs energy was introduced to explain criteria of spontaneity in terms of system.
- Since ; energy = useful work + randomness energy

$H = G + TS$

$\boxed{G = H - TS}$ ...(i)

So the function that takes both enthalpy and entropy of system into account is called Gibbs energy.

- Gibbs energy is an extensive property and state function.
- Absolute value of G can't be measured but change can be measured, So we discuss (ΔG)

Gibbs Energy

$\Delta G = G_{\text{final}} - G_{\text{initial}}$

From eq. (i) $\boxed{\Delta G = \Delta H - T\Delta S}$

Where ΔG = Change in Gibb's energy

ΔH = Change in enthalpy

ΔS = Change in entropy

Relation between Gibb's energy change and non expansion work or useful work :

FLOT : $\Delta E = q + W$

If, work is done by the system, then, $\Delta E = q - W$ ....(i)

According to Gibb's, system does both expansion and non expansion work.

$\therefore \quad W = W_{\text{expansion}} + W_{\text{non expansion}}$

$W = P\Delta V + W_{\text{non expansion}}$

Put W in equation (i)

$\Rightarrow \quad \Delta E = q - (P\Delta V + W_{\text{non expansion}})$

$q = \Delta E + P\Delta V + W_{\text{non expansion}}$

$q = \Delta H + W_{\text{non expansion}}$ $(\because \Delta H = \Delta E + P\Delta V)$

$T\Delta S = \Delta H + W_{\text{non expansion}}$ $(\because \Delta S = q/T)$

$W_{\text{non expansion}} = T.\Delta S - \Delta H$ $(\because \Delta G = \Delta H - T\Delta S)$

$\Rightarrow \quad \boxed{W_{\text{non expansion}} = -\Delta G}$ or $\boxed{W_{\text{useful}} = -\Delta G}$

The decrease in Gibb's energy of system is equal to the non expansion work or useful work.

Relation in between ΔG of system and ΔS_{total} or Gibb's energy change and spontaneity :

$\because \quad \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

Let system releases heat at constant temperature T and pressure P.

$\therefore \quad q = q_P = \Delta H$

$$\left.\begin{aligned} -q_{\text{system}} &= +\, q_{\text{surroundings}} \\ \Rightarrow \quad -\Delta H_{\text{system}} &= +\, \Delta H_{\text{surroundings}} \end{aligned}\right\}$$

$$\Delta S_{\text{surr.}} = \frac{\Delta H_{\text{surr.}}}{T}$$

$$\Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{sys}}}{T}$$

$$\because \quad \Delta S_{\text{total}} = \Delta S_{\text{sys.}} + \left(\frac{-\Delta H_{\text{sys}}}{T}\right)$$

$T\Delta S_{\text{total}} = T\Delta S_{\text{sys.}} - \Delta H_{\text{sys.}}$

$T\Delta S_{\text{total}} = -(\Delta H_{\text{sys.}} - T\Delta S_{\text{sys.}})$

$T\Delta S_{\text{total}} = -\Delta G_{\text{sys.}}$

or $\boxed{\Delta G_{\text{sys.}} = -T\Delta S_{\text{total}}}$

(i) If, $\Delta S_{\text{total}} = +ve$ $\Rightarrow \Delta G_{\text{system}} = -ve$ $\Rightarrow$ spontaneous process

(ii) If, $\Delta S_{\text{total}} = -ve$ $\Rightarrow \Delta G_{\text{system}} = +ve$ $\Rightarrow$ non spontaneous process

(iii) If, $\Delta S_{\text{total}} = 0$ $\Rightarrow \Delta G_{\text{system}} = 0$ $\Rightarrow$ process is at equilibrium.

$\Delta_r H$	$\Delta_r S$	$\Delta_r G$	Description
–	+	–	Reaction spontaneous at all temperature
–	–	–	(at low T) Reaction spontaneous at low temperature
–	–	+	(at high T) Reaction nonspontaneous at high temperature
+	+	+	(at low T) Reaction nonspontaneous at low temperature
+	+	–	(at high T) Reaction spontaneous at high temperature
+	–	+	(at all T) Reaction nonspontaneous at all temperatures

Relationship between standard Gibb's energy change ($\Delta G°$) and Equilibrium constant (K_{eq}) :-

For a reaction $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$\Delta G = \Delta G° + RT\ \ell nQ$

At equilibrium, $\Delta G = 0$ and $Q = K_{eq}$

$0 = \Delta G° + RT\ \ell n\ K_{eq}$

∴ $\Delta G^o = -RT \ln K_{eq}$ ...(i)

or $\Delta G^o = -2.303\ RT\ \log_{10} K_{eq}$ ...(ii)

from equation (i)

$$\ln K_{eq} = -\frac{\Delta G^o}{RT}$$

∴ $K_{eq} = e^{-\Delta G^o/RT}$ ...(iii)

Illustration 25:

For a certain reaction the change in enthalpy and change in entropy are 40.63 kJ mol^{-1} and 100 JK^{-1}. What is the value of ΔG at 27°C and indicate whether the reaction is possible or not ?

Solution:

We know that :

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

$T = 27 + 273 = 300K$

$\Delta H = 40.63 \times 10^3\ J\ mol^{-1} = 40630\ J\ mol^{-1}$

$\Delta S = 100\ JK^{-1}$

$\Delta G = 40630 - 300 \times 100 = 40630 - 30000 = +\ 10630\ J$

Positive value of ΔG indicates that the reaction is not possible.

Illustration 26:

For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 J mol^{-1} and -105 J mol^{-1} K^{-1} respectively. Find out whether this reaction is spontaneous or not.

Solution:

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

$= -\ 11700 - 298 \times (-\ 105) = +\ 19590\ J$

ΔG = + ve, so reaction is non-spontaneous.

Illustration 27:

Calculate the equilibrium constant for the reaction given below at 400K.

If $\Delta H° = 77.2 kJmol^{-1}$ and $\Delta S° = 122 JK^{-1} mol^{-1}$

$PCl_{5(g)} \longrightarrow PCl_{3(g)} + Cl_{2(g)}$

Solution:

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = 77200 - 400 \times 122 = 28400$ J

$\Delta G^0 = -2.303 RT \log K_c$

or $28400 = -2.303 \times 8.31 \times 400 \log K_c$

or $K_c = 1.958 \times 10^{-4}$

Illustration 28:

For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H = -95.4$ kJ and $\Delta S = -198.3$ Jk^{-1}. Calculate the temperature at which the reaction will proceed in forward direction.

Solution:

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

$\because$ At equilibrium $\Delta G = 0$

$\therefore \Delta H = T\Delta S$

so $T = \dfrac{-95.4 \times 1000 \text{ J}}{-198.3 \text{ JK}^{-1}} = 481$ K

For this reaction ΔH is –ve and ΔS is –ve, so it will be spontaneous at low temperature.

$\therefore$ Below 481K the reaction would be spontaneous.

Illustration 29:

Enthalpy and entropy changes of a reaction are 40.63 kJ mol^{-1} and 108.8 J K^{-1} mol^{-1} respectively. Analyse the feasibility of the reaction at 27°C.

Solution:

$\Delta H = 40.63$ kJ mol^{-1} = 40630 J K^{-1} mol^{-1}

$\Delta S = 108.8$ J K^{-1} mol^{-1}

T = 27°C = 27 + 273 = 300 K

Now $\Delta G = \Delta H - T\Delta S$

$= 40630 \text{ J mol}^{-1} - (300 \text{ K}) \times (108.8 \text{ J K}^{-1} \text{ mol}^{-1})$

$\Delta G = 7990 \text{ J mol}^{-1}$.

Since ΔG is positive, the reaction is not feasible in the forward direction.

Illustration 30:

For a certain reaction the change in enthalpy and change in entropy are 40·63 kJ mol^{-1} and 100 JK^{-1}. Show that at 27°C the reaction is possible or not.

Solution:

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

$\Delta G = 40.63 - 300 \times 100 \times 10^{-3}$

$\Delta G = +10{\cdot}630$ kJ

ΔG is positive so reaction is not possible.

Illustration 31:

Zinc reacts with dilute hydrochloric acid to give hydrogen at 17°C. The enthalpy of the reaction is – 12.55 kJ mol^{-1} and entropy change is 5JK^{-1} mol^{-1} for the reaction. Calculate the free energy change and predict whether the reaction is spontaneous or not.

Solution:

Given $\Delta H = -12.55\ kJmol^{-1}$ and $\Delta S = 5\ JK^{-1}\ mol^{-1}$

T= 17+273 = 290 K

Applying $\Delta G = \Delta H - T\Delta S$

$$= -12.55\ \frac{kJ}{mol} - 290K \times \frac{5}{1000}\ \frac{kJ}{Kmol}$$

$$= -12.55 - 1.45 = -14\ \frac{kJ}{mol}$$

Since ΔG is negative, the reaction will be spontaneous

Illustration 32:

For a reaction both ΔH and ΔS are positive. Under what condition will the reaction occur spontaneously?

Solution:

The reaction will occurs spontaneously only when $T\Delta S > \Delta H$.

$\Delta G = \Delta H - T\Delta S = (+) - T\ (+)$

For ΔG to be negative, $T\Delta S$ must be $> \Delta H$

Illustration 33:

Which of the following are state function ?

(i) q **(ii) Entropy** **(iii) Gibb's energy** **(iv) H** **(v) w**

Solution:

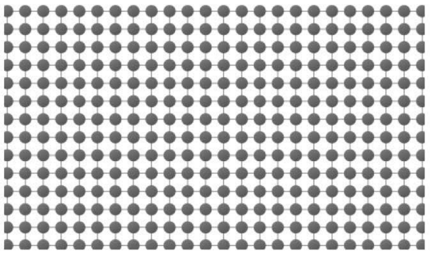
Ans. (ii), (iii) and (iv)

Third Law of Thermodynamics (TLOT)

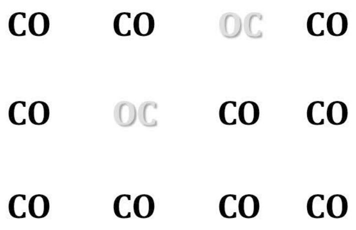
At zero kelvin (absolute zero temperature), the entropy of pure perfect crystalline solid is taken as zero.

Exceptions :

(i) NO, N_2O (ii) CO, CO_2 (iii) Mixture of isotopes (iv) Ice



Perfect Crystal ⇒ S = 0



CO Crystal ⇒ S ≠0

Introduction :

Thermochemistry is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or chemical reaction takes place within the system.

Depending upon the conditions under which the reaction is carried out, the quantity of heat transferred is related to energy or enthalpy change due to changes of states which occur in the system.

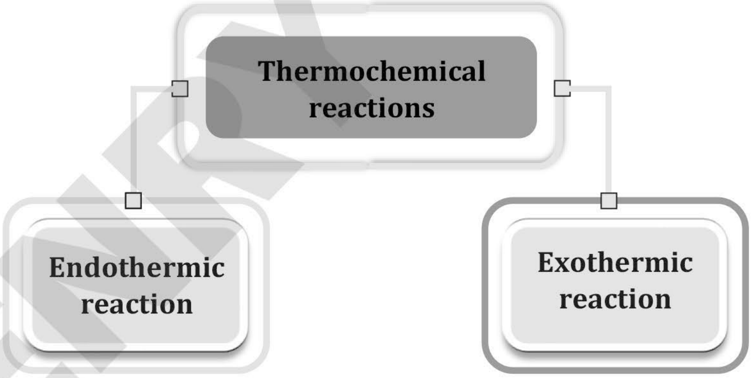
In this chapter we will introduce enthalpies of some specific reactions. Like, Enthalpy of formation (ΔH_f), Enthalpy of combustion (ΔH_{comb}), Bond dissociation enthalpy (ΔH_{BDE}) & Enthalpy of Neutralisation ($\Delta H_{neutralization}$)

Thermochemical Reaction :

The balanced chemical reaction which give information about the physical states of reactants & products and heat change is called as thermo chemical reaction.

eg. $2KClO_{3(s)} \longrightarrow 2KCl_{(s)} + 3O_{2(g)}$, $\Delta H = + x$ Cal

Thermo chemical reactions are of 2 type:



(i) Endothermic reaction :

The reaction which absorbs heat is called as endothermic reaction.

$$\boxed{\Delta H = +ve}$$

$\Delta H = H_P - H_R = +ve$ i.e. $\boxed{H_P > H_R}$

(a) Stability of reactant > Stability of product because more heat is required to break the bonds of reactant.

(b) The product formed in the endothermic reaction is called an endothermic compound.

(c) If more heat is absorbed then the product formed in the reaction will be less stable or the reactant is more stable.

Representation of endothermic reaction :

$A + B + x\ Cal \longrightarrow C + D$ (endo)

$A + B \longrightarrow C + D - x\ Cal$ (endo)

$A + B \longrightarrow C + D, \Delta H = +x\ Cal$ (endo)

Examples :

(I) Dissociation reactions (mostly)

(II) Fusion reactions

(III) Vaporization reactions

(IV) Sublimation reactions

(V) Photosynthesis

$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2, \Delta H = +ve$

(ii) Exothermic reaction :

The reaction in which heat is evolved is called as an exothermic reaction.

$\boxed{\Delta H = -ve}$ $\Delta H = H_P - H_R = -ve$ i.e. $\boxed{H_P < H_R}$

(a) Stability of reactant < Stability of product because less heat is required to break the bonds of reactant.

(b) The product formed in the exothermic reaction is called an exothermic compound.

(c) If more heat is released then the product formed in the reaction will be more stable or the reactant is less stable.

Representation of exothermic reaction.

$A + B \longrightarrow C + D + x\ Cal$ (exo)

$A + B - x\ Cal \longrightarrow C + D$ (exo)

$A + B \longrightarrow C + D, \ \Delta H = -x\ Cal$ (exo)

Examples :

(I) Combustion reactions

(II) Neutralisation reactions

(III) Respiration reaction

eg. $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$

(IV) Formation $\nearrow$ endo $\searrow$ exo(generally)

Exceptions of formation reaction:

$$\left[\begin{array}{l} S + 2S \rightarrow CS_2 \\ \frac{1}{2}N_2 + \frac{3}{2}Cl_2 \rightarrow NCl_3 \\ N_2 + O_2 \rightarrow NO / N_2O / NO_2 / N_2O_4 \\ O_2 + F_2 \rightarrow OF_2 / O_2F_2 \end{array}\right] \Delta H = +ve \text{ (endothermic)}$$

★ Golden Key Points ★

(i) If conditions are not given, then ΔH is considered to be ΔH°.

(ii) If thermochemical reaction is multiplied by a coefficient then, ΔH of reaction is also multiplied by that coefficient.

e.g. $H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O\ (\ell)$ $\Delta H = -285\ \text{kJ mol}^{-1}$

$2H_2(g) + O_2 \longrightarrow 2H_2O\ (\ell)$ $\Delta H = -2 \times 285\ \text{kJ}$

(iii) If reaction is reversed, then numerical value of ΔH remains same but sign is changed.

$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O\ (\ell)$ $\Delta H = -285\ \text{kJ mol}^{-1}$

$H_2O\ (\ell) \longrightarrow H_2(g) + \frac{1}{2}\ O_2(g)$ $\Delta H = +285\ \text{kJ mol}^{-1}$

Heat of Reaction or (Enthalply of Reaction) or (ΔH_R) :

The amount of heat evolved or absorbed when number of moles of the reactant according to the balanced chemical reaction had completely reacted is called as heat of reaction.

Example : $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$, $\Delta H_R =$ ✓

$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{(g)}$, $\Delta H_R =$ ✗

$H_{2(g)} + O_{2(g)} \longrightarrow H_2O_{2\ (g)}$, $\Delta H_R =$ ✓

Note : Heat of reaction at constant pressure is ΔH and heat of reaction at constant volume is ΔE.

Factors affecting heat of reaction :

(i) Reaction condition :

The chemical reactions are carried out at constant temperature with either pressure or volume constant. At constant pressure $q_p = \Delta H_{reaction}$

At constant volume $q_v = \Delta E_{reaction}$

$$\Delta H = \Delta E + \Delta n_g RT$$

(ii) Quantity of reactant :

Example : $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H_1 = -x$ kCal mol^{-1}

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H_2 = 2 \times (-x$ kCal)

Note: If equation is multiplied by a coefficient then value of ΔH is also multiplied by that coefficient.

(iii) Physical state of products and reactants :

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$ $\Delta H = -285.8$ kJ mole^{-1}

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -242$ kJ/mole^{-1}

If the physical state of product is different then the value of ΔH is different.

Note : For H_2O (liq.), ΔH is more negative in comparison to the formation of H_2O(vap.) because when vapours convert into liquid then some heat is released.

(iv) Allotropic form : (Physical nature of reactant)

$C_{graphite} + O_2 \longrightarrow CO_2$ $\Delta H_R = -393.5$ kJ mole^{-1}

$C_{diamond} + O_2 \longrightarrow CO_2$ $\Delta H_R = -399.5$ kJ mole^{-1}

(v) Temperature :

Effect of temperature on heat of reaction is given by **Kirchoff equation**

(i) at constant pressure : $\dfrac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_{Pm}$

$\Delta C_{Pm} = \Sigma(C_{Pm})_P - \Sigma(C_{Pm})_R$

ΔH_{T_1} = Heat of reaction at T_1 temperature

ΔH_{T_2} = Heat of reaction at T_2 temperature

(ii) at constant volume : $\dfrac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_{Vm}$

$\Delta C_{Vm} = \Sigma(C_{Vm})_P - \Sigma(C_{Vm})_R$

Types of Heat of Reaction :

(A) Heat of formation, Enthalpy of formation (ΔH_f) or ($\Delta_f H$) :

It is the enthalpy change when one mole of a substance is formed from its elements in their most abundant naturally occurring form or in their standard and stable state form (also called reference states).

The reference state of oxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of formation are :

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) \qquad \Delta H_f \quad ✓$$

$$\frac{1}{2} H_2(g) + \frac{1}{2} N_2(g) + \frac{3}{2} O_2(g) \longrightarrow \underset{1\,mole}{HNO_3} \qquad \Delta H_f \quad ✓$$

$$Na(s) + \frac{1}{2} O_2(g) + \frac{1}{2} H_{2(g)} \longrightarrow \underset{1\,mole}{NaOH} \qquad \Delta H_f \quad ✓$$

APPLICATION OF ΔH_f :

Calculation of ΔH of any general reaction.

Let us consider a general reaction $aA + bB \rightarrow cC + dD$

$$\Delta H_{reaction} = \Sigma \Delta H_{f(products)} - \Sigma \Delta H_{f(reactant)}$$

$$= \left[c\Delta H_{f(C)} + d\Delta H_{f(D)}\right] - \left[a\Delta H_{f(A)} + b\Delta H_{f(B)}\right]$$

Golden Key Points

- Standard condition means, P = 1 atm, T = 25°C or 298 K
  Standard heat of formation is represent by $\Delta H_f°$.
- If no condition is given then value of ΔH_f is considered as $\Delta H_f°$.
- Standard heat of formation of all the elements in stable standard state is taken to be zero.
- The reference state of commonly used elements are

Elements	Reference state	
C	$C_{(graphite)}$	
S	$S_{8(Rhombic)}$	(Rhombic sulphur is energy wise more stable as compared to monoclinic sulphur)
P	$P_{4(white)}$	
O	$O_{2(g)}$	
H	$H_{2(g)}$	
Br	$Br_{2(\ell)}$	
Metal	$M_{(s)}$[except $Hg_{(\ell)}$]	

- The formation reaction may be exothermic or endothermic.

Illustration 34:

Since enthalpy of elements in their natural state is taken as zero, the value of ΔH_f of compounds :

(1) is always negative **(2) is always positive**

(3) may be positive or negative **(4) is zero**

Solution:

Ans. (3)

Illustration 35:

The enthalpy of formation of ammonia at 298K is given as $\Delta H_f^\circ = -46.11$ kJ per mol of $NH_3(g)$. To which of the following equation does this value apply ?

(1) $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ **(2)** $N(g) + 3H(g) \longrightarrow NH_3(g)$

(3) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ **(4)** $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(\ell)$

Solution:

Ans. (1)

Illustration 36:

Which of the following equation represents the standard heat of formation ?

(1) $C(\text{diamond}) + 2H_2(g) \longrightarrow CH_4(g)$ **(2)** $C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g)$

(3) $C(\text{diamond}) + 4H(g) \longrightarrow CH_4(g)$ **(4)** $C(\text{graphite}) + 4H(g) \longrightarrow CH_4(g)$

Solution:

Ans. (2)

Illustration 37:

Which of the following reaction defines ΔH_f° ?

(1) $C_{(\text{diamond})} + O_2(g) \longrightarrow CO_2(g)$

(2) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \longrightarrow HF(\ell)$

(3) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

(4) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

Solution:

Ans. (2)

Illustration 38:

How much heat will be required at constant pressure to form 1.28 kg of CaC_2 from CaO(s) & C(s)?

Given :

$\Delta_f H^\circ (CaO, s) = -152$ **kCal mol^{-1}**

$\Delta_f H^\circ (CaC_2, s) = -14$ **kCal mol^{-1}**

$\Delta_f H^\circ (CO, g) = -26$ **kCal mol^{-1}**

(1) + 112 kCal **(2) 224 kCal** **(3) 3840 kCal** **(4) 2240 kCal**

Solution:

$CaO(s) + 3C(s) \longrightarrow CaC_2(s) + CO(g)$

$\Delta_f H^\circ = (-14 - 26) - (-152) = +112$ kCal mol^{-1}

Total heat required = $\left(\frac{1280}{64}\right) \times 112$

$\Rightarrow$ 2240 kCal

Illustration 39:

The $\Delta_f H°$ (N_2O_5, g) in kJ mol^{-1} on the basis of the following data is :

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\quad$ $\Delta_r H° = -114$ kJ mol^{-1}

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$ $\quad$ $\Delta_r H° = -102.6$ kJ mol^{-1}

$\Delta_f H°$ (NO,g) = 90.2 kJ mol^{-1}

(1) 15.1 (2) 30.2 (3) – 36.2 (4) none of these

Solution:

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$ $\quad$ $\Delta_f H° = 90.2$

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\quad$ $\Delta_r H° = 90.2 \times 2$ ... (1)

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\quad$ $\Delta_r H° = -114$ ... (2)

$2NO_2(g) + \frac{1}{2}O_2(g) \longrightarrow N_2O_5(g)$ $\quad$ $\Delta_r H° = \frac{-102.6}{2} = -51.3$ ... (3)

From Equations (1) + (2) + (3)

$N_2(g) + \frac{5}{2}O_2(g) \longrightarrow N_2O_5(g)$ $\quad$ $\Delta_f H°(N_2O_5, g) = 15.1$ kJ mol^{-1}

Illustration 40:

Calculate $\Delta H°$ for $2Al_{(s)} + Fe_2O_3 \longrightarrow 2Fe_{(s)} + Al_2O_3$ given that standard enthalpy of Fe_2O_3 and Al_2O_3 are –196.5 and –399.1 kCal.

Solution:

$\Delta H^0_{\text{Reaction}} = \Sigma\Delta H_P° - \Sigma\Delta H_R°$

$= \left[2\times\Delta H^0_{Fe(s)} + \Delta H^0_{Al_2O_3}\right] - \left[2\times\Delta H^0_{Al(s)} + \Delta H^0_{Fe_2O_3}\right]$

$= 2 \times 0 + (-399.1) - [2 \times 0 + (-196.5)]$

$\Delta H^0_{\text{Reaction}} = -202.6$ kCal

Illustration 41:

The heat of formation of the compound in the following reaction is :

$H_{2(g)} + Cl_{2(g)} \longrightarrow 2HCl_{(g)} + 44$ kCal

(1) –44 kCal mol^{-1} (2) – 22 kCal mol^{-1} (3) +11 kCal mol^{-1} (4) –88 kCal mol^{-1}

Solution:

Ans. (2)

For the formation of 1 mol of HCl from elements $\Delta H_f° = \frac{-44}{2} = -22$ kCal

Heat of combustion (ΔH_{comb}) :

Amount of heat evolved when 1 mole of substance is completely burnt (or oxidised) in excess of oxygen.

Example :

$\underset{1\text{mole}}{C_{\text{graphite}}} + O_2 \longrightarrow CO_2,$	ΔH_{comb} ✓	and	ΔH_f	✓
$\underset{1\text{mole}}{C_{\text{diamond}}} + O_2 \longrightarrow CO_2,$	ΔH_{comb} ✓	and	ΔH_f	✗
$\underset{1\text{mole}}{C} + \frac{1}{2}O_2 \longrightarrow CO,$	ΔH_{comb} ✗	and	ΔH_f	✓
$\underset{1\text{mole}}{CO} + \frac{1}{2}O_2 \longrightarrow CO_2,$	ΔH_{comb} ✓	and	ΔH_f	✗

Note :

(I) Heat of combustion reaction is always exothermic

(II) If conditions are not given then ΔH_{comb} considered as ΔH°_{comb}.

(III) If in a reaction heat of combustion of reactants and products are given then heat of that reaction can be measured as follows

$$\Delta H = \Sigma(\Delta H_{comb})_R - (\Delta H_{comb})_P$$

Application of Heat of Combustion :

Calorific value or fuel value (C.V.) :

The amount of heat evolved when 1 g of a substance (food or fuel) is completely burnt (or oxidised)

$$\text{Calorific value} = \frac{\Delta H_{comb}}{\text{Molecular weight}}$$

Unit :- kJ g^{-1} or kCal g^{-1}

★ Golden Key Points ★

- Heat of combustion reaction is always exothermic
- If conditions are not given then ΔH_{comb} is considered as ΔH°_{comb}.
- Maximum value of calorific value = Maximum efficiency or best fuel
- H_2 has the highest calorific value (150 kJ/g) but it is not used as domestic or industrial fuel due to some technical problems.

Illustration 42:

Calculate the heat of formation of Benzene. The reaction is given as $6C(s) + 3H_2(g) \rightarrow C_6H_6(\ell)$ and –3268, –393.5 and –285.8 kJ mol^{-1} are the heats of combustion of benzene, heat of formation of CO_2 and heat of formation of $H_2O(\ell)$ respectively.

Solution:

Target reaction, $6C(s) + 3H_2(g) \rightarrow C_6H_6(\ell)$

Given

(i) $C_6H_6(\ell) + \frac{15}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$ $\Delta H = -3268$ kJ

(ii) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

(iii) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$; $\Delta H = -285.8$ kJ

6 × eq. (ii) + 3 × eq. (iii) – eq. (i)

$\Delta H = 6 \times -393.5 + 3 \times -285.8 - (-3268) = +49.6$ kJ mol^{-1}

Illustration 43:

The heats of formation of CO_2 (g) and $H_2O(\ell)$ are – 97 and – 68 kCal mol^{-1}. The heat of combustion of benzene is –783 kCal mol^{-1}. What will be the heat of formation of benzene?

Solution:

Given :

(i) $C_6H_6(\ell) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$; $\Delta H = -783$ kCal mol^{-1}

(ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -97$ kCal mol^{-1}

(iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$; $\Delta H = -68$ kCal mol^{-1}

Target reaction

$6C(s) + 3H_2(g) \longrightarrow C_6H_6(\ell)$; $\Delta H = -3$ kCal mol^{-1}

6 × eq. (ii) + 3 × eq. (iii) – eq. (i)

$\Delta H = 6 \times -97 + 3 \times -68 - (-783) = -3$ kCal mol^{-1}

Illustration 44:

Calculate the enthalpy of combustion of ethylene (gas) to form CO_2 (gas) and H_2O (gas) at 298 K and 1 atmospheric pressure. The enthalpies of formation of $CO_2(g)$, $H_2O(g)$ and $C_2H_4(g)$ are –393.7, –241.8, + 52.3 kJ per mol respectively.

Solution:

We are given :

(i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.7$ kJ mol^{-1}

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$; $\Delta H = -241.8$ kJ mol^{-1}

(iii) $2C(s) + 2H_2(g) \longrightarrow C_2H_4(g)$; $\Delta H = +52.3$ kJ mol^{-1}

Target reaction

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(g)$, $\Delta H = ?$

2 × Equation (i) + 2 × Equation (ii) – Equation (iii) gives

$\Delta H = 2(-393.7) + 2(-241.8) - (52.3) = -1323.3$ kJ mol^{-1}

Illustration 45:

1 mole of methanol, when burnt in oxygen, gives out –723 kJ mol^{-1} heat. If 1 mole of oxygen is used what will be the amount of heat evolved?

(1) 723 kJ **(2) 964 kJ** **(3) 482 kJ** **(4) 241 kJ**

Solution:

Ans. (3)

$CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$, $\Delta H = -723$ kJ

with 1 mole of O_2, $\Delta H = \frac{-723 \times 2}{3} = -482$ kJ

Illustration 46:

Combustion of methane :

(1) is an exothermic reaction
(2) is an endothermic reaction
(3) requires a catalyst
(4) gives H2

Solution:

Ans. (1)

Combustion is always exothermic.

Illustration 47:

The heat evolved in the combustion of glucose is given by the equation

$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g), \Delta H = -680$ kCal

The weight of $CO_2(g)$ produced when 170 kCal of heat is evolved in the combustion of glucose is

(1) 264 g
(2) 66 g
(3) 11 g
(4) 44 g

Solution:

Ans. (2)

Evolution of 680 kCal is accompanied by $CO_2 = 6 \times 44 = 264$ g

Evolution of 170 kCal is accompanied by $CO_2 = \frac{264}{680} \times 170 = 66$ g

Illustration 48:

Find out the calorific value of Glucose

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$; $\Delta H = -2900$ kJ mol^{-1}

Solution:

$\because$ Heat evolved from 1 mol glucose = 2900 kJ

or Heat evolved from 180 gram glucose = 2900 kJ

$\therefore$ Heat evolved from 1 gram glucose $= \frac{2900}{180} = 16.11$ kJ g^{-1}

or another method $\quad$ $\text{C.V.} = \frac{\Delta H_{comb}}{M_w} = \frac{2900}{180} = 16.11$ kJ g^{-1}

Illustration 49:

Enthalpy of combustion of a substance is always :

(1) > 0
(2) > 0
(3) < 0
(4) < 0

Solution:

Ans. (4)

Illustration 50:

The heat change for a reaction : $CO(g) + \frac{1}{2}O_2 \longrightarrow CO_2(g)$ refers to

(1) enthalpy of formation of carbon dioxide

(2) enthalpy of combustion of carbon dioxide

(3) enthalpy of vapourisation

(4) enthalpy of combustion of carbon monoxide

Solution:

Ans. (4)

Heat of Neutralization (ΔH_{neut}) :

The heat evolved when one equivalent of an acid is completely neutralized by one equivalent of a base in dilute solution is called as heat of neutralization.

$$SA + SB \longrightarrow \text{Salt + Water}$$

$$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl + H_2O$$

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

$$\boxed{H^+ + OH^- \rightarrow H_2O}$$

Note :

(i) When one equivalent of SA is neutralized by one equivalent of SB, then heat evolved remains constant and its value is – 13.7 kCal/equivalent or – 57.2 kJ equivalent^{-1}.

eg.

SA		SB		
HCl (aq)	+	NaOH (aq)	$\longrightarrow$	$NaCl + H_2O + 13.7$ kCal
NV = 1 eq.		NV = 1 eq.	$\longrightarrow$	$\Delta H = -13.7$ kCal
NV = 2 eq.		NV = 2 eq.	$\longrightarrow$	$\Delta H = 2\,(-13.7)$ kCal
NV = 3 eq.		NV = 3 eq.	$\longrightarrow$	$\Delta H = 3\,(-13.7)$ kCal
NV = 4 eq.		NV = 5 eq. = (4 + 1) eq.	$\longrightarrow$	$\Delta H = 4\,(-13.7)$ kCal
NV = 5 eq. = (3+2)eq		NV = 3 eq.	$\longrightarrow$	$\Delta H = 3\,(-13.7)$ kCal

(ii) If one of the acid or base or both are weak, then heat of neutralization is usually less than –13.7 kCal eq^{-1} or –57.3 kJ eq^{-1} because some part of the heat released in neutralization is absorbed to dissociate the weak electrolyte completely.

eg. $\overset{WA}{CH_3COOH}(aq)+\overset{SB}{NaOH}(aq) \rightarrow CH_3COONa(aq) + H_2O;\ \Delta H = -13.4$ kCal eq^{-1}

Exception : For a reaction $HF + NaOH \rightarrow NaF + H_2O$; $\Delta H = -16.7$ kCal; this is because of hydration of F^- ion.

Illustration 51:

Heat of neutralisation of an acid by a base is maximum when :

(1) Both the acid and base are weak

(2) Both the acid and base are strong

(3) The acid is strong and the base is weak

(4) The acid is weak and the base is strong

Solution:

Ans. (2)

Heat of neutralisation is maximum (57.2 kJ eq^{-1} or 13.7 kCal eq^{-1}) when both acid and base are strong.

Illustration 52:

If $H^+ + OH^- \longrightarrow H_2O + 13.7$ kCal, then heat of complete neutralisation of 1 gm mol of H_2SO_4 with base in excess will be :

(1) –13.7 kCal **(2) –27.4 kCal** **(3) –6.85 kCal** **(4) –3.425 kCal**

Solution:

Ans. (2)

Moles of H_2SO_4 = 1 mol

g eq. of H_2SO_4 = moles × V.F. = 1 × 2 = 2 g eq.

Heat evolve due to 2 g eq. = – 13.7 × 2 = – 27.4 kCal

Illustration 53:

200 cm³ of 0.1 M H_2SO_4 is mixed with 150 cm³ of 0.2 M KOH. Find the value of evolved heat.

Solution:

H_2SO_4	KOH
eq. = NV = (0.1 × 2) × 0.2	(0.2 × 1) × (0.15)
= 0.04	= 0.03

Heat liberated by 1 eq. = 57.2 kJ

So heat liberated by 0.03 eq. = 57.2 × 0.03 = 1.7 kJ

Heat of Hydrogenation ($\Delta H_{Hydrogenation}$) :

The heat evolved during the complete hydrogenation of one mol unsaturated organic compound into its saturated compound is called as heat of hydrogenation.

Unsaturated organic compound $\xrightarrow{\text{Change}}$ Saturated organic compound

(= or ≡ Bond) **(– Bond)**

$C_2H_2 + 2H_2 \longrightarrow C_2H_6,$ ΔH_{hydro} ✓

$C_2H_2 + H_2 \longrightarrow C_2H_4,$ ΔH_{hydro} ✗

$C_2H_4 + H_2 \longrightarrow C_2H_6,$ ΔH_{hydro} ✓

Note : Heat of hydrogenation is exothermic process.

Heat of Atomization (ΔH_{atom}) :

The amount of heat required to dissociate 1 mol substance into gaseous atoms is called as heat of atomization.

Example : $\frac{1}{2}H_{2(g)} \longrightarrow 1\ H_{(g)}$ ΔH_{atom} ✓

$H_{2(g)} \longrightarrow 2\ H_{(g)}$ ΔH_{atom} ✓

$\frac{1}{2}Cl_{2(g)} \longrightarrow 1\ Cl_{(g)}$ ΔH_{atom} ✗

$Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ ΔH_{atom} ✓

Note : It is an endothermic reaction.

Heat of Transformation :

(i) **Heat of fusion (ΔH_{fusion}) :** The required amount of heat to convert 1 mole solid into liquid at its melting point is called as heat of fusion.

Example : $1\ H_2O_{(s)} \longrightarrow H_2O_{(l)}$; $\Delta\ H_{fusion}$ ✓

Note : Heat of fusion is always endothermic reaction i.e. (Δ H = + ve)

(ii) **Heat of vaporization (ΔH_{Vapour}) :** The required amount of heat to convert 1 mole liquid into gas at its boiling point is called as heat of vaporization.

Example : $1\ H_2O_{(\ell)} \longrightarrow H_2O_{(g)}$; $\Delta\ H_{Vapour}$ ✓

Note : Heat of vaporization is always endothermic reaction i.e. (Δ H = +ve)

(iii) Heat of sublimation (ΔH_{Sub}) :

The required amount of heat to convert 1 mole solid into gas at a certain temperature is called as heat of sublimation.

Example : $H_2O_{(s)} \longrightarrow H_2O_{(g)}$; ΔH_{Sub} ✓

Note : Heat of sublimation is always endothermic reaction i.e. (ΔH = + ve)

Illustration 54:

The enthalpy change for the process $C_{(s)} \longrightarrow C_{(g)}$ corresponds to the enthalpy of

(1) fusion (2) vapourization (3) combustion (4) sublimation

Solution:

Ans. (4)

Solid $\longrightarrow$ gas, is sublimation.

Bond Energy / Bond Dissociation Energy :

The required amount of energy to dissociate **one mole gaseous bond** into separate **gaseous atoms** is called as **bond dissociation energy.**

Example :

$1H - H_{(g)} \longrightarrow 2H_{(g)}$ ΔH_{H-H} ✓

$1Cl - Cl_{(g)} \longrightarrow 2Cl_{(g)}$ ΔH_{Cl-Cl} ✓

$1H - Cl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}$ ΔH_{H-Cl} ✓

$1H - Cl_{(g)} \longrightarrow H^+_{(g)} + Cl^-_{(g)}$ ΔH_{H-Cl} ✗

$1H - Cl_{(g)} \longrightarrow \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)},$ ΔH_{H-Cl} ✗

$1H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)}$ ΔH_{H-O} ✗

Golden Key Points

- The **bond energy** may be defined as the **average** amount of energy required to dissociate one mole gaseous bond into separate gaseous atoms.
- Bond dissociation process is an endothermic process.
- If bond energy of various bonds present in the reactants and products are given then ΔH of that reaction can be calculate as follows.

  $\Delta H = \Sigma(B.E.)_R - \Sigma(B.E.)_P$
- **In the case of poly atomic molecule** we calculate the average bond energy.

  $(BE)_{av} = \text{Average bond energy} = \dfrac{\text{Total energy required with all bonds}}{\text{Number of bond dissociation}}$

  Example : $H-O-H_{(g)} + 112\text{ kJ} \longrightarrow H-O_{(g)} + H_{(g)}$

  $H-O_{(g)} + 108\text{ kJ} \longrightarrow H_{(g)} + O_{(g)}$

  $(BE)_{av} = \text{Average bond energy} = \dfrac{112+108}{2} = 110\text{ kJ mol}^{-1}$

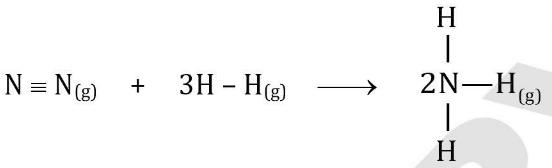
Illustration 55:

Given the bond energy of N ≡ N, H – H and N – H bonds are 945, 436 and 391 kJ mol⁻¹ respectively, the enthalpy of the reaction $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$ is :

(1) – 93 kJ **(2) 102 kJ** **(3) 90 kJ** **(4) 105 kJ**

Solution:

Ans. (1)



$$N\equiv N_{(g)} \quad + \quad 3H-H_{(g)} \longrightarrow 2\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{N}}}}-H_{(g)}$$

945 + 3 × 436	2 × (3 × 391)
= 2253 kJ	= 2346 kJ

$\Delta H = \Sigma\,(B.E.)_R - \Sigma\,(B.E.)_P = 2253 - 2346 = -93$ kJ

Illustration 56:

The enthalpy changes at 298 K in successive breaking of O – H bonds of H – O – H are

$H_2O_{(g)} \longrightarrow H_{(g)} + OH_{(g)}, \ \Delta H = 498\text{ kJ mol}^{-1}$

$OH_{(g)} \longrightarrow H_{(g)} + O_{(g)}, \ \Delta H = 428\text{ kJ mol}^{-1}$

The bond enthalpy of the O – H bond is

(1) 498 kJ mol⁻¹ **(2) 463 kJ mol⁻¹** **(3) 428 kJ mol⁻¹** **(4) 70 kJ mol⁻¹**

Solution:

Ans. (2)

$(B.E.)_{av} = \dfrac{498+428}{2} = 463$ kJ

Illustration 57:

The required heat for dissociation of 1 mol H_2O into its atoms (H and oxygen) is $\Delta H_{Dis.}$. Then calculate the bond energy of O – H bond.

$H_2O\,(g) \rightarrow O(g) + 2H(g);\ \Delta H_{Dissociation}$

Solution:

$H - O - H(g) \longrightarrow O(g) + 2H(g); \Delta H_{Dissociation}$

$\because$ required energy for breaking the 2 mol O – H bond = $\Delta H_{Dis.}$

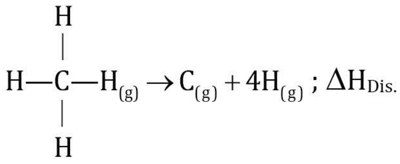
$\therefore$ required energy for 1 mole = $\frac{\Delta H_{Dis.}}{2}$; $\Delta H_{O-H} = \frac{\Delta H_{Dis.}}{2}$

Illustration 58:

Calculate the bond energy of C – H Bond in methane.

Solution:

$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)} \quad ; \Delta H_{Dis.}$

or 

$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H_{(g)} \rightarrow C_{(g)} + 4H_{(g)}\ ; \Delta H_{Dis.}$$

$\because$ Bond energy of 4 mol C – H= ΔH_{Dis}

$\therefore$ Bond energy of 1 mol C – H bond = $\frac{\Delta H_{Dis.}}{4}$

Illustration 59:

The energy change of reaction $C_2H_{6(g)} \longrightarrow 2C_{(g)} + 6H_{(g)}$ is X kJ. The bond energy of C – H bond is:

(1) $\frac{X}{6}$ kJ mol^{-1} (2) $\frac{X}{3}$ kJ mol^{-1} (3) X kJ /mol^{-1} (4) unpredictable from data

Solution:

Ans. (4)

If we know C–C bond energy than only we can calculate C–H bond energy using given data.

Illustration 60:

$CuSO_4(\ell) + 5H_2O(s) \longrightarrow CuSO_4.\,5H_2O(s)$; $\Delta H = -x$ kJ

The value of ΔH represents :

(1) enthalpy of solution of copper (II) sulphate

(2) enthalpy of hydration of copper (II) sulphate

(3) enthalpy of hydrolysis of copper (II) sulphate

(4) lattice energy of copper (II) sulphate

Solution:

Ans. (2)

Illustration 61:

The bond energy of hydrogen is 103 kCal mol^{-1}. This means that :

(1) 103 kCal are required to break 6.023×10^{23} gaseous H_2 molecules into gaseous atoms

(2) 103 kCal are required to break the bonds in one gram of hydrogen

(3) 103 kCal are required to break one bond to form two atoms of hydrogen

(4) 103 kCal are required to break one mole of gaseous hydrogen molecules into ions.

Solution:

Ans. (1)

Heat of Hydration (ΔH_{hydra}) :

Amount of heat evolved when **one mole** of anhydrous salt combines with fixed number of water molecules to convert into its specific hydrated crystal is called as heat of hydration.

Example :

- $1\ CuSO_4(s) + 5H_2O(\ell) \longrightarrow CuSO_4.5H_2O(s)$ $\Delta H = -$ ve

  anhydrous salt hydrated salt

- $1\ MgSO_4(s) + 7H_2O(\ell) \longrightarrow MgSO_4.7H_2O(s)$ $\Delta H = -$ ve

  anhydrous salt hydrated salt

- $1\ CaCl_2(s) + 6H_2O(\ell) \longrightarrow CaCl_2.6H_2O(s)$ $\Delta H = -$ ve

  anhydrous salt hydrated salt

Special Note : Heat of hydration is exothermic

Heat of Solution ($\Delta H_{sol.}$) :

Amount of heat absorbed or evolved when **one mol** of substance is dissolved in such a large volume of solvent that further addition of solvent does not produce any more heat change is called as **'Heat of solution'**.

Example 1: $1\ CuSO_{4(s)} + aq \longrightarrow CuSO_4(aq)$ $\Delta H_{solution}$ ✓

Example 2: $MgSO_{4(s)} + 7H_2O(\ell) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

$MgSO_4.7H_2O(s) + aq \longrightarrow MgSO_4(aq)$ $\Delta H_{solution}$ ✓

Special Note : Heat of solution may be endothermic or exothermic.

Illustration 62:

The heat of solution of anhydrous $CuSO_4(s)$ is –15.9 kCal mol^{-1} and that of $CuSO_4.5H_2O(s)$ is 2.8 kCal mol^{-1}. Calculate the heat of hydration of $CuSO_4(s)$.

Solution:

Given $CuSO_4(s) + aq. \longrightarrow CuSO_4(aq)$ $\Delta H = -15.9$ kCal ....(i)

$CuSO_4.5H_2O(s) + aq. \longrightarrow CuSO_4(aq)$ $\Delta H = +2.8$ kCal ....(ii)

Subtracting Eq. (ii) from Eq.(i)

$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s)$; $\Delta H = -15.9 - 2.8 = -18.7$ kCal

Heat of hydration of $CuSO_4 = -18.7$ kCal mol^{-1}

Laws of Thermochemistry :

(I) Lavoisier and Laplace Law :

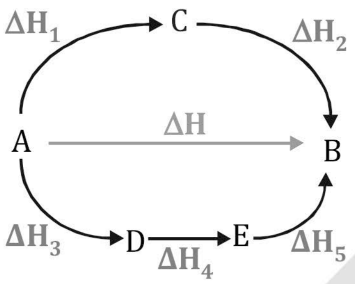
Enthalpy of formation of compound is **numerically equal** to the enthalpy of decomposition of that compound with **opposite sign**.

Example : $C + O_2 \longrightarrow CO_2, \quad \Delta H = -94$ kCal

$CO_2 \longrightarrow C + O_2, \quad \Delta H = +94$ kCal

(II) Hess Law of Constant Heat Summation :

The heat change in a complete chemical reaction always remain same whether reaction completes in one step or more.

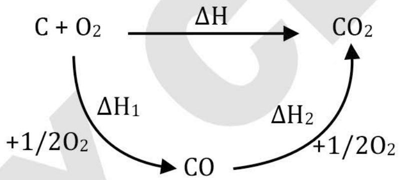


$$\Delta H = \Delta H_1 + \Delta H_2$$

or $$\Delta H = \Delta H_3 + \Delta H_4 + \Delta H_5$$

or $$\Delta H = \Delta H_1 + \Delta H_2 = \Delta H_3 + \Delta H_4 + \Delta H_5$$

Example:



$$\Delta H = \Delta H_1 + \Delta H_2$$

Golden Key Points

- Heat change of a reaction does not depend on the **number of steps** used in the reaction.
- Heat change of a reaction does not depend on **intermediate position**, it depend only on initial and final state.
- Heat change of a chemical reaction does not depend on **time of reaction**.

Illustration 63:

Single step reaction $A \rightarrow B$; $\Delta H = ?$

Multi step reaction to produce B from A is given

$$A \xrightarrow{\Delta H_1} C \xrightarrow{\Delta H_2} D \xrightarrow{\Delta H_3} E \xrightarrow{\Delta H_4} B$$

Solution:

According to Hess's law $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4$