Unit 6

Thermodynamics

- **Thermodynamics** is a branch of science which deals with the study of interconversion of different forms of energies and their quantitative relationships.

INTERNAL ENERGY

- The total energy stored in a substance (or a system) is called its internal energy. It is the sum of various energies associated with atoms and molecules such as translational energy (E_t), vibrational energy (E_v), rotational energy (E_r), potential energy (E_p), electronic energy (E_e), nuclear energy (E_n), chemical energy (E_c), etc.

  Thus U or $E = E_t + E_v + E_r + E_p + E_e + E_n + E_c$

- It is a state function whose absolute value can not be determined because all kind of energies associated with it can not be measured. However change in internal energy (ΔU) can be calculated.

  $\Delta U = U_2 - U_1$ or $\Delta U = U_{product} - U_{reactant}$

  Where U_2 and U_1 represent the internal energy of final and initial state respectively.

FIRST LAW OF THERMODYNAMICS

- It is a law of conservation of energy which states that energy can neither be created nor destroyed, although it can be converted from one form to another. This obviously means that total energy of the universe remains constant.

  Mathematically : ΔE or $\Delta U = q + W$ or $q = \Delta U - W$

  - If W is work of expansion $i.e.$, $W = -P\Delta V$ then $\Delta U = q - P\Delta V$ or $q = \Delta U + P\Delta V$

  - For isothermal irreversible expansion $\Delta U = 0$ thus $q = -W = P\Delta V$

  - For isothermal reversible expansion $\Delta U = 0$ thus

  $$q = -W = 2.303\, nRT \log\frac{V_2}{V_1}$$

  - For adiabatic processes, $q = 0$ thus $\Delta U = W_{adiabatic}$

  We know $\dfrac{dU}{dT} = C_V \Rightarrow dU = C_V dT$

  Thus $W_{adiabatic} = C_V dT = C_V (T_2 - T_1)$

  - For isochoric process, $\Delta V = 0$, thus $q = \Delta U$

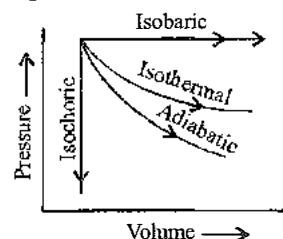- **Graphical representation of thermodynamic processes**

Illustration 1

10 g of argon gas is compressed isothermally and reversibly at a temperature of 27° C from 10 litre to 5 litre. Calculated q, W and ΔU for this process.

($R = 2.0$ cal K^{-1} mol^{-1}, atomic weight of Argon = 40)

Soln.:

$$W_{iso,\,rev} = -2.303\, nRT \log\frac{V_2}{V_1} = -2.303\, nRT \log\frac{5}{10}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300 \log\frac{5}{10} = 103.9 \text{ cal.}$$

For isothermal process $\Delta U = 0$

From 1st law of thermodynamics, $\Delta U = q + W$

$\therefore$ $q = -W = -103.9$ cal

ENTHALPY

- Total heat content of the system at constant pressure is known as its enthalpy.

  $H = U + PV$

  If H_2 is the enthalpy in final state and H_1 in initial state, then

  $\Delta H = H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1)$

  $\boxed{\Delta H = \Delta U + P\Delta V}$

- Enthalpy change represents the heat absorbed or evolved by the system at constant pressure. It is a state function.

- **Sign convention :** For exothermic reaction ($i.e.$, heat released during the reaction) ΔH is negative $i.e.$, $\Delta H < 0$. Whereas for endothermic reaction ($i.e.$, heat absorbed during the reaction), ΔH is positive $i.e.$, $\Delta H > 0$.

- **Relationship between ΔH and ΔU**

  We know that $\Delta H = \Delta U + P\Delta V$

  ΔV is the change in volume $i.e.$, $\Delta V = V_2 - V_1$

$\therefore \quad \Delta H = \Delta U + P(V_2 - V_1) = \Delta U + (PV_2 - PV_1)$

For ideal gases $PV = nRT$

Thus we have $PV_1 = n_1RT$

and $\qquad PV_2 = n_2RT$

Where n_1 and n_2 are number of moles of gaseous reactants and products respectively.

Hence we can have $\Delta H = \Delta U + (n_2RT - n_1RT)$

$\qquad\qquad\qquad = \Delta U + (n_2 - n_1)RT$
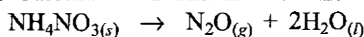
$$\boxed{\Delta H = \Delta U + \Delta n_g RT}$$

When $\Delta n_g = 0$, then $\qquad \Delta H = \Delta U$

When $\Delta n_g > 0$, then $\qquad \Delta H > \Delta U$

When $\Delta n_g < 0$, then $\qquad \Delta H < \Delta U$

Illustration 2

The molar heat of formation of $NH_4NO_{3(s)}$ is -367.54 kJ and those of $N_2O_{(g)}$ and $H_2O_{(l)}$ are $+81.46$ kJ and -285.78 kJ respectively at $25°$ C and 1.0 atmospheric pressure. Calculate ΔH and ΔU for the reaction,

$\qquad NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(l)}$

Soln.: $\qquad NH_4NO_{3(s)} \rightarrow N_2O_{(g)} + 2H_2O_{(l)}$

ΔH_f (kJ) $\quad -367.54 \qquad 81.46 \quad 2 \times -285.78$

$\Delta H = \Delta H_{f \text{ (Products)}} - \Delta H_{f \text{ (Reactants)}}$

$\quad = [2 \times (-285.78) + 81.46] - (-367.54)$

$\quad = -122.56$ kJ $= -122.56 \times 10^3$ J

$\Delta n_g = n_p - n_r = 1 - 0 = 1$

$\Delta H = \Delta U + \Delta n_g RT \Rightarrow \Delta U = \Delta H - \Delta n_g RT$

$\Delta U = -122.56 \times 10^3 - 1 \times 8.314 \times 298 = -125.03 \times 10^3$J

$\qquad\qquad\qquad\qquad\qquad\qquad = -125.03$ kJ

Heat Capacity (C)

● Heat capacity is the amount of heat required to raise the temperature of a system by one degree.

$$\boxed{C = \frac{q}{\Delta T}}$$

where q is the amount of heat supplied and ΔT is the increase in temperature.

➤ Heat capacity at constant volume

$$\boxed{C_V = \left(\frac{dU}{dT}\right)_V}$$

➤ Heat capacity at constant pressure

$$\boxed{C_P = \left(\frac{dH}{dT}\right)_P}$$

For one mole of an ideal gas, $\boxed{C_P - C_V = R}$

Where R is gas constant. Thus $C_P > C_V$.

● **Specific heat capacity :** It is the amount of heat required to raise the temperature of 1 gram of the substance by one degree.

● **Molar heat capacity :** It is the amount of heat required to raise the temperature of 1 mole of the substance by one degree.

Hess's Law of Constant Heat Summation

● This law was presented by Hess in 1840. According to the law, if a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change is always the same.

Thus, the total enthalpy change of a chemical reaction depends on the initial and final stages only.
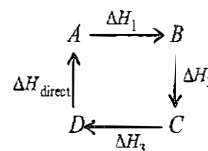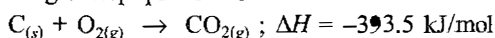

Total enthalpy change from A to D,

$\Delta H_{total} = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H_{total} + \Delta H_{direct} = 0$
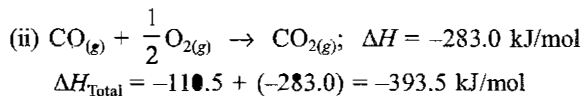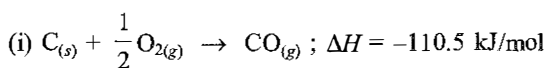
i.e. $\Delta H_{total} = -\Delta H_{direct}$

For example, formation of CO_2 from C in two different manners involves a total heat change of -393.5 kJ/ mol

Single step process :

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -393.5$ kJ/mol

Two step process :

(i) $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$; $\Delta H = -110.5$ kJ/mol

(ii) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta H = -283.0$ kJ/mol

$\Delta H_{Total} = -110.5 + (-283.0) = -393.5$ kJ/mol

STANDARD ENTHALPY OF REACTION

● A substance is said to be in standard state when it is present in its most stable state at 298 K under a pressure of one atmosphere.

● **Heat of formation or enthalpy of formation :** The heat evolved or absorbed when 1 mole of a substance is formed from its elements is called heat of formation.

➤ **Standard enthalpy of formation:** The enthalpy of formation depends upon the conditions of formation, i.e., temperature, pressure and physical state (gas, solid or liquid) or allotropic state of the reactants. If all substances of the chemical reaction are in their standard state (i.e, at 25°C or 298 K and 1 atmospheric pressure), the heat of formation or enthalpy of formation is called standard heat of formation or standard enthalpy of formation. It is denoted by $\Delta E°_f$ (volume constant) or $\Delta H°_f$ (pressure constant).

● **Heat of combustion or enthalpy of combustion :** The amount of heat change when 1 mole of a substance is completely burnt in excess of oxygen or air is called heat of combustion. It is generally denoted by ΔH_c.

$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$;

$\qquad\qquad\qquad\qquad \Delta H = \Delta H_c = -1367.4$ kJ
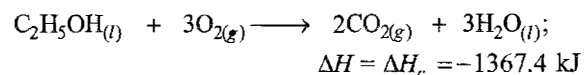
It may be noted that the heat of combustion (ΔH_c) is always negative because heat is always evolved during combustion.

➤ **Calorific Value of Foods and Fuels :** It is defined as the amount of heat produced in calories (or

joules) when one gram of a substance (food or fuel) is completely burnt.

The calorific value is usually expressed in kcal per gram or kilojoules per gram (1 kcal = 4.184 kJ).

● **Heat of solution :** The heat of solution is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.
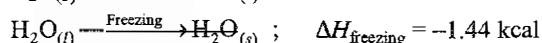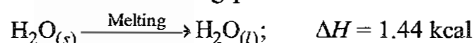
$$KCl_{(s)} + aq \rightarrow KCl_{(aq)} ; \Delta H = 4.4 \text{ kcal}$$
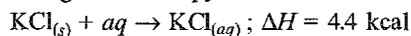
● **Heat of ionization :** The heat required to ionise the weak acid or the weak base is known as the enthalpy of ionisation.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

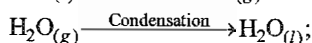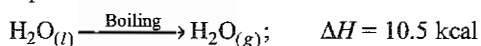or $\Delta H^o = -55.43 \text{ kJ mol}^{-1}$
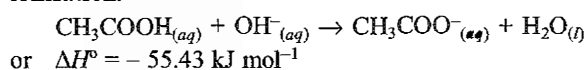
For a weak acid or a weak base, the enthalpy of neutralisation is not the same but less than -57.32 kJ. It is because of the fact that these acid or base are not completely ionised in solution. Some of the heat is consumed in ionising these acid and base.

Hence $\Delta H^o_{ionisation} = -55.43 + 57.32 = +1.89 \text{ kJ mol}^{-1}$.

● **Heat of fusion or enthalpy of fusion :** The heat change when 1 mole of a solid substance is converted into its liquid state at its melting point is called heat of fusion.

$$H_2O_{(s)} \xrightarrow{\text{Melting}} H_2O_{(l)}; \quad \Delta H = 1.44 \text{ kcal}$$

$$H_2O_{(l)} \xrightarrow{\text{Freezing}} H_2O_{(s)} ; \quad \Delta H_{freezing} = -1.44 \text{ kcal}$$

● **Heat of vaporisation or enthalpy of vaporisation :** The heat change when 1 mole of a liquid is converted into gaseous state at its boiling point is called heat of vaporisation.
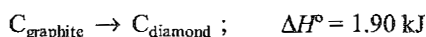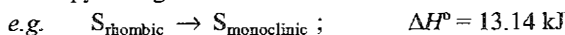
$$H_2O_{(l)} \xrightarrow{\text{Boiling}} H_2O_{(g)}; \quad \Delta H = 10.5 \text{ kcal}$$

$$H_2O_{(g)} \xrightarrow{\text{Condensation}} H_2O_{(l)};$$

$$\Delta H_{condensation} = -10.5 \text{ kcal}$$

● **Heat of sublimation or enthalpy of sublimation :** The heat change when one mole of a solid is directly converted into its gaseous state at a temperature below its melting point is called heat of sublimation.
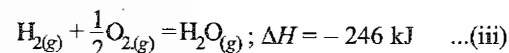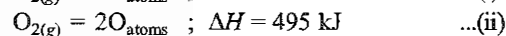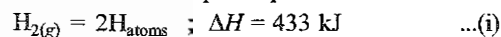
$$I_{2(s)} \rightarrow I_{2(g)}; \Delta H = 14.9 \text{ kcal}$$
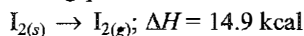
● **Heat of transition :** The enthalpy change when one mole of an allotropic form changes to another. It may be transitions from solid to liquid (fusion), liquid to vapour (vaporisation), solid to vapour (sublimation) and change from one crystalline form to another crystalline form (polymorphic transition). For example, in the transition of sulphur (rhombic) to sulphur (monoclinic), the enthalpy change is 13.14 kJ.
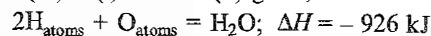
e.g. $\quad S_{rhombic} \rightarrow S_{monoclinic} ; \quad \Delta H^o = 13.14 \text{ kJ}$

$\quad C_{graphite} \rightarrow C_{diamond} ; \quad \Delta H^o = 1.90 \text{ kJ}$

● **Heat of atomization :** The enthalpy change required to convert one mole of an element from its normal state at 298 K and one atmosphere pressure into free atoms.

$$H_{2(g)} = 2H_{atoms} ; \Delta H = 433 \text{ kJ} \quad ...(i)$$

$$O_{2(g)} = 2O_{atoms} ; \Delta H = 495 \text{ kJ} \quad ...(ii)$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)} ; \Delta H = -246 \text{ kJ} \quad ...(iii)$$

Then (iii) – (i) – 1/2 × (ii) gives;

$$2H_{atoms} + O_{atoms} = H_2O; \Delta H = -926 \text{ kJ}$$

● **Heat of hydration :** The heat or enthalpy of hydration of salt is the change in heat content ΔH when one mole of an anhydrous substance combines with requisite number of mole of water to form the hydrated salt.

e.g. $CuSO_{4(s)} + 5H_2O_{(l)} \rightarrow CuSO_4 \cdot 5H_2O_{(s)};$
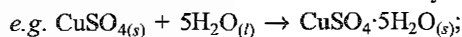
$$\Delta H^o = 78.22 \text{ kJ}$$

BOND ENERGY AND BOND DISSOCIATION ENERGY

● The amount of energy required to break a bond is called bond dissociation energy or simply bond energy.

● The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, *i.e.* to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy.

The combustion of 1 mol of ethane

$$C_2H_{6(g)} + 7/2 O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$$

$$2O = C = O_{(g)} + 3H - O - H_{(g)}$$
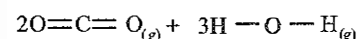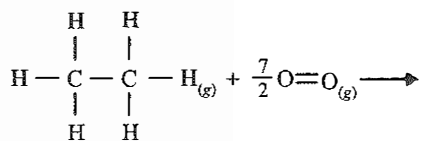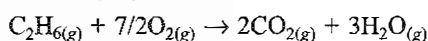
Bonds broken : 6 moles C – H bonds, 1 mol C – C bonds, 7/2 moles of O = O bonds
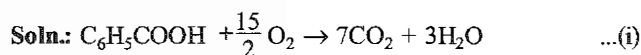
Bonds formed : 4 moles C = O bonds, 6 moles O – H bonds

$$\Delta H = \left[(6 \times 413) + (348) + \left(\frac{7}{2} \times 495 \right) \right] - [(4 \times 799) + (6 \times 463)]$$

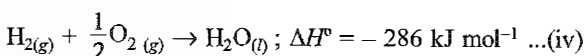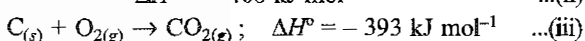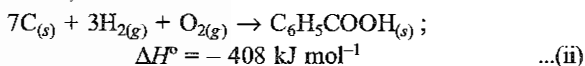$$= 4558 - 5974 = -1416 \text{ kJ (The reaction is exothermic.)}$$

Illustration 3

At 300 K, the standard enthalpies of formation of $C_6H_5COOH_{(s)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ are -408, -393 and -286 kJ mol^{-1}, respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume. ($R = 8.314$ J mol^{-1} K^{-1})

Soln.: $C_6H_5COOH + \frac{15}{2} O_2 \rightarrow 7CO_2 + 3H_2O \quad ...(i)$

Given,

$$7C_{(s)} + 3H_{2(g)} + O_{2(g)} \rightarrow C_6H_5COOH_{(s)} ;$$
$$\Delta H^o = -408 \text{ kJ mol}^{-1} \quad ...(ii)$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} ; \quad \Delta H^o = -393 \text{ kJ mol}^{-1} \quad ...(iii)$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} ; \Delta H^o = -286 \text{ kJ mol}^{-1} ...(iv)$$

In order to obtain eqn (i) operate $7 \times$ (iii) $+ 3 \times$ (iv) $-$ (i)

$\Delta H° = [-393 \times 7 - 286 \times 3 + 408]$

$\therefore \quad \Delta H° = -3201 \text{ kJ mol}^{-1}$

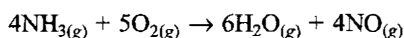Also $\Delta H_P = \Delta H_V + \Delta nRT$

$\therefore \quad -3201 = \Delta H_V + (-1/2) \times 8.314 \times 10^{-3} \times 300$

$(\because \Delta n = -1/2 \text{ and } R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1})$

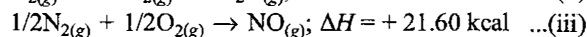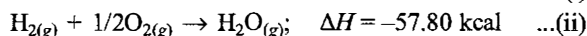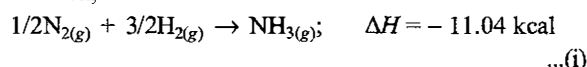$\therefore \quad \Delta H_V = -3201 + 1.2471 = -3199.7529 \text{ kJ mol}^{-1}$

Illustration 4

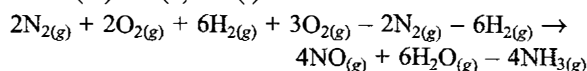Calculate the heat of reaction (ΔH_r) when ammonia is oxidised.

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

Standard enthalpies of formation ($\Delta H_f°$) at 25°C for $NH_{3(g)}$, $H_2O_{(g)}$ and $NO_{(g)}$ are -11.4, -57.80 and $+21.60$ kcal/mol respectively.

Soln.: Given,

$1/2N_{2(g)} + 3/2H_{2(g)} \rightarrow NH_{3(g)}; \quad \Delta H = -11.04 \text{ kcal}$ ...(i)

$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}; \quad \Delta H = -57.80 \text{ kcal}$ ...(ii)

$1/2N_{2(g)} + 1/2O_{2(g)} \rightarrow NO_{(g)}; \Delta H = +21.60 \text{ kcal}$ ...(iii)

To obtain the required reaction operate

4 (iii) + 6 (ii) − 4 (i)

$2N_{2(g)} + 2O_{2(g)} + 6H_{2(g)} + 3O_{2(g)} - 2N_{2(g)} - 6H_{2(g)} \rightarrow$
$4NO_{(g)} + 6H_2O_{(g)} - 4NH_{3(g)}$

$\Delta H = 21.60 \times 4 - 57.80 \times 6 + 11.04 \times 4 \text{ kcal}$

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

$\Delta H = -216.24 \text{ kcal}$

$\Delta H_r = -216.24 \text{ kcal}.$

Illustration 5

Find ΔH of the following reaction,
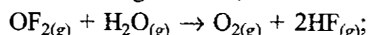
$$OF_{2(g)} + H_2O_{(g)} \rightarrow O_{2(g)} + 2HF_{(g)};$$

average bond energies of O − F, O − H, O═O, H − F are 44, 111, 118 and 135 kcal/mol respectively.

Soln.: $OF_{2(g)} + H_2O_{(g)} \rightarrow O_{2(g)} + 2HF_{(g)}$

(i) Bond breaking (endothermic) ΔH_1

$F - O - F \rightarrow O_{(g)} + 2F_{(g)}; \Delta H = +2 \times 44$

$H - O - H \rightarrow O_{(g)} + 2H_{(g)}; \Delta H = +2 \times 111$
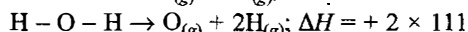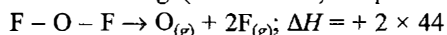
$\therefore \quad \Delta H_1 = 2 \times 44 + 2 \times 111 = +310 \text{ kcal}$

(ii) Bond formation (exothermic) ΔH_2

$O + O \rightarrow O_2; \Delta H = -118$

$2[H + F \rightarrow H - F]; \quad \Delta H = -2 \times 135$
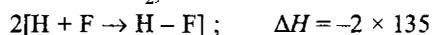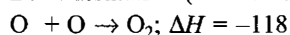
$\Rightarrow \Delta H_2 = -118 + (-2 \times 135) = -388 \text{ kcal}$

Now using Hess's Law;

$\Delta H_{reaction} = H_1 + H_2 = 310 + (-388) = -78 \text{ kcal}$

ENTROPY

- Entropy is a measure of randomness or disorderness of the system, denoted by S. Entropy is a state function as it does not depend on path, depends only on final and initial stage.
- The absolute value of entropy cannot be calculated, only change in entropy can be calculated.

$$\Delta S = \frac{q}{T} \text{ J K}^{-1} \text{ mol}^{-1}$$

- **Entropy changes**

Entropy changes	Formula
Fusion : When 1 mole of a solid substance changes to liquid at melting temperature (T_m).	$\Delta S_{fus} = \dfrac{\Delta H_{fus}}{T_m}$
Vaporisation : Entropy when 1 mole of a liquid substance changes into vapour state at boiling temperature (T_b).	$\Delta S_{vap} = \dfrac{\Delta H_{vap}}{T_b}$
Sublimation : When 1 mole of solid directly changes into gas at temperature (T).	$\Delta S_{sub} = \dfrac{\Delta H_{sub}}{T}$
During isothermal reversible expansion of a gas	$\Delta S = R \ln\dfrac{V_2}{V_1} = R \ln\dfrac{P_1}{P_2}$
During adiabatic reversible change	$\Delta S = 0,$ i.e. isoentropic process
When P = constant	$\Delta S_P = C_P \ln\dfrac{T_2}{T_1}$
When V = constant	$\Delta S_V = C_V \ln\dfrac{T_2}{T_1}$

GIBBS FREE ENERGY

- Free energy of a system is defined as the maximum amount of energy available to the system during a process which can be converted into useful work. Hence free energy is a measure of capacity to do useful work. Useful work means work other than that of expansion.

$$\boxed{\Delta G = -W_{max}}$$

It is denoted by G, and given mathematically as

$$G = H - TS$$

where H is the enthalpy, T is absolute temperature and S is entropy of the system.

For initial state $G_1 = H_1 - TS_1$

For final state $G_2 = H_2 - TS_2$

$\therefore \quad \Delta G = G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$
$= (H_2 - H_1) - T(S_2 - S_1)$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

➢ If electrical work is involved, then electrical work $= nFE$

where n is number of electrons involved in cell reaction

F is Faraday and, E is EMF of the cell.

$-\Delta G = nFE$ or $\boxed{\Delta G = -nFE}$

➢ If standard state is maintained i.e., 298 K and 1 atm pressure during the reaction, then,

$-\Delta G° = nFE°$ or $\boxed{\Delta G° = -nFE°}$

where $\Delta G°$ is standard free energy change.
$E°$ is standard EMF of the cell.

- **Standard free energy of formation (ΔG_f°)** : It is the free energy change which takes place when one mole of a compound is formed from its elements in their standard state. It is taken as zero for the formation of pure elements. Standard free energy of formation is used to calculate standard free energy of reaction.

$$\Delta G^\circ_{Reaction} = \Sigma \Delta G^\circ_{f(Products)} - \Sigma \Delta G^\circ_{f(Reactants)}$$

- **Standard free energy change and equilibrium constant** : Standard free energy change and equilibrium constant are related to each other in the following manner :

$$\Delta G^\circ = - RT \ln K$$

or $$\Delta G^\circ = -2.303\ RT \log K$$

- **Spontaneity based on Gibb's free energy** : A process is said to be spontaneous when it take place by itself or after proper initiation under a given set of conditions.

- For a reaction to be spontaneous ΔG must be negative
  If $\Delta G = 0$, process is in equilibrium and
  If $\Delta G = $ positive, process is non-spontaneous.

- **Relation between ΔH, ΔS, ΔG and spontaneity of a reaction**

S. No.	Sign of ΔH	Sign of ΔS	$\Delta G = \Delta H - T\Delta S$	Remarks
1.	−ve	+ve	Always −ve	Spontaneous at all temperatures
2.	+ve	−ve	Always +ve	Non - spontaneous at all temperatures
3.	+ve	+ve	+ve at low temperature, −ve at high temperature	Non - spontaneous at low temperature, spontaneous at high temperature
4.	−ve	−ve	−ve at low temperature, +ve at high temperature.	Spontaneous at low temperature, non - spontaneous at high temperature

Illustration 6

$A + B \rightarrow C + D$
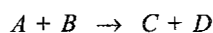
$\Delta H = - 10000$ J mol^{-1} ; $\Delta S = - 33.3$ J K^{-1} mol^{-1}

(i) At what temperature the reaction will occur spontaneously from left to right?

(ii) At what temperature, the reaction will reverse?

Soln.: At equilibrium $\Delta G = 0$

Since, $\Delta G = \Delta H - T\Delta S$, so at equilibrium

$$T = \frac{\Delta H}{\Delta S} = \frac{-10000}{-33.3} = 300.3\,K$$

(i) For left to right spontaneity, ΔG should be negative. For ΔG to be negative, temperature must be less than 300.3 K *i.e.,* $T < 300.3$ K.

(ii) For reverse reaction *i.e.,* right to left spontaneity, ΔG should be positive. For ΔG to be positive, temperature must be more than 300.3 K *i.e.,* $T > 300.3$ K.

SECOND LAW OF THERMODYNAMICS

- The drawbacks of first law of thermodynamics are answered by 2nd law of thermodynamics. There are many statements for this 2nd law.
  - All spontaneous processes are thermodynamically irreversible.
  - It is impossible to convert heat completely into equivalent amount of work without leaving some effect elsewhere.
  - Without the help of an external agency, heat can not by itself flow from a cold body to hot body.
  - The entropy of the universe is continuously increasing.

THIRD LAW OF THERMODYNAMICS

- This law states that entropy of all perfectly crystalline solids approaches zero at absolute zero (zero Kelvin). Entropy is a measure of disorder, hence it can be said that at absolute zero a perfectly crystalline solid has a perfect order of its constituent particles.

- **Application** : This law helps in calculating absolute entropies of pure substances at any temperature.

$$\Delta S = S_T - S_0 = \int_0^T \frac{C_P\,dT}{T} = C_P \ln T = 2.303\ C_P \log T$$

where S_T and S_0 are entropies at T K and 0 K respectively.

As $S_0 = 0$ (according to third law)

$$\therefore\quad S = \int_0^T \frac{C_P\,dT}{T}.$$

The value can be calculated graphically.