CHAPTER 06

THERMODYNAMICS

LECTURE 01

- Thermo → heat
- Dynamics → energy
- It is a branch of chemistry that deals with study of heat energy and quantitative relationship between heat and different forms of energy.

Some term related to thermodynamics :

1. **System :**

   It is a specified part of the universe which is taken for studies, known as system.

2. **Surrounding :**

   The remaining part of the universe which is not consider for studies, known as surrounding.

3. **Boundary :**

   The region separating system from surrounding is called boundary.

4. **Closed system, open system & isolated system.**

   (i) Open System

   System which allows exchange of matter as well as energy/heat with the surrounding is called open system.

   E.g. Evaporation of water in an open vessel.

   (ii) Closed System

   System which can exchange heat but not matter with the surrounding is called a closed system.

   e.g., Heating of water in a closed metallic vessel.

   (iii) Isolated System.

   System which can neither exchange heat nor matter with the surrounding is called an isolated system.

e.g., Let us consider some water and sodium metal in an insulated vessel.

$Na + H_2O \rightarrow NaOH + H_2 \uparrow$

It is highly exothermic.

5. Homogeneous System & Heterogeneous System :

(i) System which has uniform composition & identical properties throughout the phase.

It is a uni-phase system.

e.g. Salt + Water.

(ii) Heterogeneous System :

System which has no uniform composition and no identical properties throughout the phase, it is called heterogeneous system.

e.g., oil + water

It has two distinct phases.

LECTURE 02

- **Macroscopic Property :**

  System which depends upon the bulk properties of the materials/substances like mass, volume, temperature, pressure surface tension, viscosity etc. are called macroscopic properties of a system.

- **Macroscopic Properties are of two types.**

  (i) Extensive properties

  (ii) Intensive Properties.

  - **Extensive Properties :**
    - A property which depends upon the amount of substances, are called extensive properties.
    - E.g. mass volume heat capacity, internal energy, enthalpy, entropy, Gibb's free energy.
  - **Intensive Properties :**

- Macroscopic properties which does not depends upon the amount of substances but depends upon the nature of substances are called intensive properties.
- E.g., pressure, temperature, density, surface tension, viscosity, refractive index electro motive force and chemical potential (E. Cell).

❖ State of a system, state variable, state function :

(i) State of a system :

- The condition of existence of a system when its macroscopic properties have definite value are called state of system.
- State of a system having initial and final state.

(ii) State Variable :

- The physical quantities required to describe state of a system is called state variable.
- e,g state variable are pressure, temperature volume etc.

(iii) State Function :

- System/macroscopic properties which depends upon the initial and final state of the system but does not depends upon the path followed, is called state function.

❖ Characteristics of state functions :

(i) If depends upon the initial and final state.

(ii) It does not depends upon the path followed.

(iii) The absolute value cannot be determined.

(iv) It has exact differential.

(v) The change in value can be calculated.

For example : $\Rightarrow ds = s_2 - s_1 = \Delta S$

dS, dH, dU

$$\int_{H_1}^{H_2} dH = H_2 - H_1 = \Delta H$$

$$\int_{U_1}^{U_2} dU = U_2 - U_1 = \Delta U$$

Where,

S - Entropy

H – Enthalpy

U – Energy

❖ **Path Function :**

- The macroscopic properties of a system which depends upon the path followed or the manner in which it takes place, is called path function.

❖ ***Thermodynamics Process :***

It is of five types :

(i) Isothermal process
(ii) Adiabatic Process
(iii) Isobaric Process
(iv) Isochoric Process
(v) Cyclic Process

(i) Isothermal Process

- Thermodynamic Process which take place at constant temperature i,e, the initial state and final state having same temperature, $\Delta T = 0$ but heat and work can be exchanged then the process is called isothermal process :

(ii) Adiabatic Process :

- Thermodynamics process in which there is no exchange of heat takesplace between system and surrounding i-e $q = 0$ but work can be exchange then the process is called Adiabatic Process.

(iii) Isobaric Process :

- Thermodynamic process which can be carried out at constant pressure in other words the system having same pressure at initial and final state, i.e, $\Delta P = 0$ but heat and work can be exchanged between system and souranding then the process is called Isobaric Process.

(iv) Isochoric Process :

- Thermodynamics process which can be carried out at constant volume, i.e, the system having same volume at initial and final state i.e. $\Delta V = 0$ but heat can be exchanged, then the process is called **Isochoric** Process.

(v) Cyclic Process :

- It is a thermodynamic process in which a system can be return back to its original position after undergoing several changes called cyclic process.

Internal Energy :

❖ **Mode of transfer of heat :**

(i) When the system having more heat energy than surrounding, the flow of heat takes place from system to surrounding this is called heat energy lost by the system.
Heat lost by the system represented by –ve sign.

(ii) When the surrounding having mode heat energy than system, now flow of heat takes place from surrounding to system, in this is case system absorb heat energy from the surrounding, which is represented by '+ve' sign.

❖ Work :

(i) Work done on the system represented by '+ve' sign and it is due to compression of gases. In this case [Page – External]

(ii) Work done by the system represented by '-ve' sign and it is due to expansion of gases. In this case [External <Pages]

❖ **Internal Energy :**

- It is sumtotal of the energy stored in a system. In other words the total energy stored in a system consdition is called internal energy.
- It is represented by 'U' or 'E'.

❖ **Characteristics of Internal energy :**

(i) It is an extensive property.

(ii) It is a state function.

(iii) It has exact differential for example $\int_{U_1}^{U_2} dU = U_2 - U_1 = \Delta U$.

(iv) The absolute value can not be determined accurately but only the difference value can be calculated.

- Internal energy means different short of energy like, virbational rotational, translation etc of a system.
- 1^{ST} law of thermodynamics :

(i) It states that energy can neither be created nor be destroyed, rather.

(ii) The sum total energy in this universe remain constant.

(iii) It can be converted from one form to another form.

(iv) The total energy of an isolated system is taken as constant.

(v) Mathematical expression of Pr law of thermodynamics :

$\boxed{dU = q + w}$

Caste – 1 : When $q = +ve$

dU increases.

Case – 2 : When $q = -ve$

dU decreases

Case – 1 : Work done on the system, $W = +ve$

$\boxed{U_2 = U_1 + q + w}$

Case – 2 : Work done by the system, $W = -ve$.

$\boxed{U_2 = U_1 + q - w}$

$\boxed{W = P\Delta V}$

When, $\Delta V = 0$, then $W = O$, it indicates no work done.

LECTURE 03

❖ Enthalpy :

- The total heat content of a system at constant pressure is knonw as enthalpy of a system. It is represented by it.
- It is also defined as the sum of the internal enerpy and product of pressure and volume in a system is called enthalpy of a system.
- Mathematically.

$\boxed{H = E + PV}$ or $\boxed{H = U + PV}$

❖ Characteristics of enthalpy :

(i) It is a state function, whose value depends upon the initial and final state and does not depends upon the path followed.

(ii) It is an extensive properties, which depends upon the amount of substances.

(iii) Absolute value of enthalpy can not be measured.

(iv) It has an exact differential.

$$\int_{H_1}^{H_2} dH = H_2 - H_1 = \Delta H$$

(v) If a system changes from its initial state to final state having internal energy E_1 and E_2 and let its volume changes from v_1 to v_2. Let H_1 and H_2 are enthalpies of initial and final state of the system.

We have,

$$H_1 = E_1 + PV_1$$

$$H_2 = E_2 + PV_2$$

$$\Rightarrow H_2 - H_1 = E_2 - E_1 + P(V_2 - V_1)$$

$$\Rightarrow \boxed{\Delta H = \Delta E + P\Delta V} \text{ ....(1)}$$

Relation between change in enthalpy change in workdone and internal energy.

From ideal gas,

$$PV = nRT$$

$$PV_1 = n_1RT$$

$$PV_2 = n_2RT$$

$$\Rightarrow P\left(V_2 - V_1\right) = \left(n_2 - n_1\right)RT$$

$\Rightarrow \boxed{P\Delta V = \Delta n_{(g)}RT}$, where

$\Delta n\left(g\right) =$ no. of gaseous moles of product no of gaseous moles of reactant.

Q. Write the relationship between ΔH & ΔE for the following chemical reactions.

(i) $PCl_{5(g)} \Rightarrow PCl_3\left(g\right) + Cl_2\left(g\right)$

(ii) $N_2\left(g\right) + 3H_2\left(g\right) \rightarrow 2NH_3\left(g\right)$

(iii) $2SO_2\left(g\right) + O_2\left(g\right) \rightarrow 2SO_3\left(g\right)$

(iv) $H_2\left(g\right) + I_2\left(g\right) \rightarrow 2HI\left(g\right)$

(v) $2H_2\left(g\right) + O_2\left(g\right) \rightarrow 2H_2O\left(l\right)$

(vi) $NH_4Cl_{(s)} \rightarrow NH_3\left(g\right) + HCl\left(g\right)$

Ans.

(i) $\Delta n_{(g)} 2 - 1$

$= +1$

$\boxed{\Delta H > \Delta E}$

(ii) $\Delta n_{(g)} = 2 - 4$

$= -2$

$\boxed{\Delta H < \Delta E}$

(iii) $\Delta n_{(g)} = 2-3$

$= -1$

$\boxed{\Delta H < \Delta E}$

(iv) $\Delta n_{(g)} = 2-2$

$= 0$

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

(v) $\Delta n_{(g)} = O-3$

$= -3$

$\boxed{\Delta H < \Delta E}$

(vi) $\Delta n_{(g)} = 2-0$

$= 2$

$\boxed{\Delta H > \Delta E}$

LECTURE 04

Enthalpy of a reaction :

The total heat energy evolved or absorbed when no. of moles of reactants react completely to produce the product is called enthalpy of a reaction.

Eg $A+B \rightarrow C+D+Q\ KJ/moles$

$\Delta H = -Q\ KJ/mole$

Similary,

$A+B+Q\ K\ Joule/mole \rightarrow C+D$.

Endothermic

$\Delta H = +Q \text{ KJ/mole}$

- In other words, the enthalpy change during a chemical reaction is called enthalpy of a reaction.

It is represented by $\Delta_f H = \sum \Delta_p H - \sum \Delta_r H$

- Standard enthalpy of reaction represented by $(\Delta r H)$.
- The change in enthalpy during a chemical reaction at standard state i.e. 1 atm pressure and at 298 K known as standard enthalpy of a reaction.
- **These are of different types :**

(i) Enthalpy of formation $\Delta_f H$ **:**

- The enthalpy change during formation of one mole of a substance or compound from its element in stable state.

  Let, $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 394$ Kj/mole.

  $$\Delta_f H = \frac{-394}{2} \text{kJ mol}^{-1}.$$

  $\Rightarrow$ Standard enthalpy of formation :

  - The enthalpy of formation at standard state i.e 1 atm pressure and at 298 K is called standard enthalpy of formation.
  - Represented by $\rightarrow (\Delta_f H^0)$.

(ii) Enthalpy of combustion $(\Delta_c H)$:

The enthalpy changed during combustion of one mole of substances completely.

e.g., $C_{(s)} + O_2(g) \rightarrow CO_2(g) + 393.5 \text{ kJ mol}^{-1}$

$\Delta_c H = -393.5 \text{ kJ/mole}$.

❖ **Standard enthalpy of combustion :**

- The enthalpy of combustion at standard state i.e. 1 atm pressure and at 298 K is called standard enthalpy of combustion.
- Represented by $(\Delta_c H^0)$

❖ **Enthalpies of transformation :**

1. **Enthalpy of fusion** $\left(\Delta_{fus}H\right)$
2. **Enthalpy of vapourisation** $\left(\Delta_{vap}H\right)$
3. **Enthalpy of sublimation** $\left(\Delta_{sub}H\right)$

1. The enthalpy changed during conversion of 1 mole of solid susbstances into its liquid at its melting point.

$$H_2O_{(s)} \xrightleftharpoons{\Delta H_{fusion}} H_2O(l)$$

2. Enthalpy of vaporisation :

$$H_2O(l) \xrightleftharpoons{\Delta H_v} H_2O\ (vapour)$$

3. Enthalpy of sublimation :

$$I_2(s) \xrightarrow{H_{sub}} I_2(vapour)$$

LECTURE 05

❖ **Hess's law of constant heat summation :**

- **Statement** → The enthalpy change during a chemical reaction remains same, whether the reaction takes place in single step or in several steps.

Let a system takes place in two way

(i) $A \xrightarrow{\Delta H} D$ (direct method)

(ii) $A \xrightarrow{\Delta H} B \xrightarrow{\Delta H_2} C \xrightarrow{\Delta H_3} D$ (In direct method)

⇒ Mathematically

$$\boxed{\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3}$$

⇒ Formation of CO_2 can be direct or indirect.

Illustration :

(i) $C_{(s)} + O_2(g) \rightarrow CO_2(g) + 393.5\ \text{kJ mol}^{-3}$ [direct]

(ii) $C_{(g)} + \frac{1}{2}O_2(g) \rightarrow CO_{(g)} + 283\ \text{kJ mol}^{-1}$

(iii) $CO(g) + \frac{1}{2}O_2 \rightarrow CO_2(g) + 110.5\ \text{kJ mol}^{-1}$ [Indirect]

$C(s) + O_2(g) \rightarrow CO_{2(g)} + 393.5\ \text{kJmol}^{-1}$

1. Calculate the enthalpy of formation of ethyl alcohol. From the following data.

(i) $C_2H_5OH_{(l)} + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$\Delta H = -1368.2\ \text{kJmol}^{-1}$

(ii) $C_{(s)} + O_2(g) \rightarrow CO_2(g)\ \ \Delta H = -393\ \text{kJ mol}^{-1}$

(iii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

$\Delta H = -286.6\ \text{kJ mol}^{-1}$

The required equation,

$$2C_{(s)} + 3H_{2(g)} + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH_{(l)} + 2\text{KJ mol}^{-1}$$

Equation 3×3

$$\Rightarrow 3H_2(g) + \frac{3}{2}O_2(g) \Rightarrow 3H_2O_{(l)} + 859.8\ \text{kJ mol}^{-1}$$

Now, adding equation $5\ \&\ 6$, we get.

$$2C + 2O_2 \rightarrow 2CO_2 + 786\ \text{kJ/mol}$$

$$3H_2 + \frac{3}{2}O_2 \rightarrow 3H_2O + 859.8\ \text{kJ/mol}$$

$$2C_{(s)} + \frac{7}{2}O_2(g) + 3H_2(g) \rightarrow 2CO_2 + 3H_2O + 1643.8\ \text{KJ mol}$$

Now, subtracting equation 7 and equation 1, we get,

$$2C_{(s)}+\frac{7}{2}O_2(g)+3H_2(g)\rightarrow 2CO_2+3H_2O+1645.8\,kJmol^{-1}$$

$$C_2H_5OH+3O_2\rightarrow 2CO_2+3H_2O+1368.8\,KJ/mol$$

$$\underset{(-)}{C_2}H_5OH\underset{(-)}{+}3O_2\rightarrow \underset{(-)}{2}CO_2\underset{(-)}{+}3H_2O\underset{(-)}{+}1368.8\,KJ/mol$$

$$2C+\frac{1}{2}O_2+3H_2\rightarrow C_2H_5OH+277.6\,KJ/mol$$

$$\boxed{\because \Delta H=-277.6\,kJ/mol}$$

02. Calculate the heat of formation of acetic acid, under the standard condition from following data 25^0C

.

(i) $(C_{(s)}+O_{2(g)}\rightarrow CO_{2(g)}+380\,kJ\,mol^{-1}$

(ii) $H_{2(g)}+\frac{1}{2}O_2(g)\rightarrow H_2O_{(l)}+275\,kJ\,mol^{-1}$

(iii) $CH_3COOH(l)+2O_2(g)\rightarrow 2CO_2(g)+2H_2O+876.6\,kJ\,mol^{-1}$

The required equation

$$2C_{(s)}+2H_{2(g)}+O_{2(g)}\rightarrow CH_3COOH+Q\,KJ\,mol^{-2}$$

Now,

$$equation1\times 2\rightarrow 2C+2O_2\rightarrow 2CO_2+760\,KJ/mol$$

$$equation2\times 2\rightarrow 2H_2+O_2\rightarrow 2H_2O+550\,KJ/mol$$

$\oplus$

$$2C+3O_2+2H_2\rightarrow 2CO_3+2H_2O+13100\,KJ/mol$$

Now, subtracting equation 4 and euations.

$$2C + 3O_2 + 2H_2 \rightarrow 2CO_2 + 2H_2O + 1310\ KJ/mol$$

$$CH_3COOH + \underset{(-)}{2O_2} \rightarrow \underset{(-)}{2CO_2} + \underset{(-)}{2H_2O} + \underset{(-)}{876.6}\ KJ/mol$$

$$2\ \ 2C + 2H_2 + O_2 \rightarrow CH_3COOH + 433.4\ KJ/mol$$

They $\boxed{\Delta H = 433.4\ KJ/mol}$

Q3. Calculate the heat of formation of benzene, given that the standard heat of combustion of benzene is -3266 KJ/mol and standard heat of formation of carbon dioxide and water $-393.1\ kJ/mol$ & -26.0 KJ/mol respectively.

Solution :

(1) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + 393.1\ kJ/mol$

(2) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} + 286\ kJ/mol$

(3) $C_6H_{6(l)} + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_8 + 3266\ KJ/mol$

Required equation,

$$6C + 3H_2 \rightarrow C_6H_6 + Q\ \ KJ/mol$$

Equation $1 \times 6\ \ = 6C + 6O_2 \rightarrow 6CO_2 + 2358.6\ KJ/mol$

Equation $11 \times 3 = 3H_2 + \frac{3}{2}O_2 \rightarrow 3H_2O + 858.0\ KJ/mol$

$\oplus$

$$6C + 3H_2 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O + 3216.6\ KJ/mol$$

Subtracting equation 4 from equation 3.

$$6C + 3H_2 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O + 3216.6\ KJ/mol$$

$$C_6H_6 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 3H_2O + 3266\ \ KJ/mol$$

(-) (-) (-) (-) (-) (-)

$$6C + 3H_2 \rightarrow C_6H_6 - 49.4\ KJ/mol$$

So, $\boxed{\Delta H = 49.4\ KJ/mol}$

4. Calculate the value of ΔH for the following equation.

(i) $CH_4(g) + 4F_2(g) \rightarrow Cl_4(g) + 4HF_{(g)}$

Given that enthalpies of formation of CH_4, CF_4 & HF are -75 KJ/mol

-680 KJ/mol and -269 Kj/mol respectively ?

Solution : $\sum \Delta H_p^\circ - \sum \overset{\circ}{\Delta} H_r$

Irreversible Process

A process is said to be irreversible if it changes rapidly such that the system does not get any change to be is in equilibrium with the surrounding. Workdone is minimum.

- **Reversible Process :**
  - Thermodynamic
  - A processs is said to be reversible process, if it changes infinitesimaly slowly so that the system all-ways in equilibrium with the surrounding.
  - Work done for a reversible process.

$$w = \int_{vi}^{vf} P_{ext} dv$$

$$\Rightarrow w = -\int_{vi}^{vf} (p_{in} \pm dp) dv$$

[$\because$ where dv and dp are small changes in volume and pressure respectively]

$$\Rightarrow w = -\int_{vi}^{vf} p_{in} dv$$ [dp are small in pressure which can be neglected]

$$\Rightarrow w = -\int_{vi}^{vf} p.dv \qquad [\because p_{in} = p]$$

$$\Rightarrow w = -\int_{vi}^{vf} \frac{nRT}{v} dv \qquad \left[\because pv = nR \Rightarrow P = \frac{nRT}{v}\right]$$

$$\Rightarrow w = -nRT \int_{vi}^{vf} \frac{dv}{v}$$

$$\Rightarrow w = -nRT \ln \frac{vf}{vi} \qquad \left[\because \int \frac{dv}{v} = \ln v\right]$$

$$\Rightarrow \boxed{w = -2.303\, nRT \, \log \frac{vf}{vi}}$$

Expansion of a gas in vaccum is called free expansion.

In free expansion.

$P_{ext} = 0$

Thus,

$$w = -\int_{vi}^{vf} P_{ext}\, dv$$

$$\Rightarrow w = -\int_{vi}^{vf} O\, dv$$

$$\Rightarrow w = +0$$

$$\Rightarrow \boxed{-w = 0}$$

[$\because$ No,work is done during free expansion of an ideal gas whether the process is reversible or irreversible]

Now, If we apply to 1st law of thermodynamics if a process is carried out at constant volume i.,e. $\Delta V = 0$,

then $\boxed{\Delta U = q_v}$

Here 'q_v' represent the heat is supplied at constant volume.

LECTURE 06

- **Heat Capacity (C)**
  - It is defined as the amount of heat required to raise temperature of a system through $1^0 C$.
  - It is represented by 'C'.
- **Specific heat**
  - It is the amount of heat required to raise 1 gram of substance through $1^0 C$.
- **Molar heat capacity :**
  - It is the amount of heat required to raise 1 mole of a substance through $1^0 C$.
- **Relationship between heat capacity at constant pressure and constant volume.**

Let Cp be the heat capacity of a system at constant pressure and Cv be the heat capacity of a system of constant volume.

So, this two can be expressed in terms of heat.

$q_v = C_v.\Delta T = \Delta U$

Similarly, $q_p = c_p.\Delta T = \Delta H$

And we have, $\Delta H = \Delta U + P\Delta V$ [For 1 mole of a substance]

$$\Rightarrow C_P.\Delta T = C_V.\Delta T + P\Delta V$$

$$\Rightarrow C_P.\Delta T = C_V.\Delta T + \Delta(PV)$$

$$\Rightarrow C_P.\Delta T = C_V.\Delta T + \Delta(RT) \qquad [\because PV = RT]$$

$$\Rightarrow (C_P - C_V)\Delta T = R\Delta T$$

$$\Rightarrow \boxed{C_P - C_V = R}$$

❖ **Entropy(s) :**

- ➢ It is defined as the measure of degree of randomness or disorderness.
- ➢ Represented by ‘S’.

Characteristics :

(i) It is a state function.

(ii) It is an extensive properties.

(iii) Its absolute value can not be measured accurately.

(iv) It has exact differential.

(v) Only the differential value can be calculated.

So, change in entropy $(\Delta S) = S_{\text{final}} - S_{\text{Initial}}$

$= S_2 - S_1$

$= S_{\text{product}} - S_{\text{reactant}}$

Change in entropy for a reversible reaction = $\boxed{\Delta S = \frac{q_{(\text{reversible})}}{T}}$

$\Rightarrow$ Factors influencing the entropy :

1. Entropy of solid < Liquid < Gas (state)

   e,g Ice $\xrightarrow{\Delta}$ water $\xrightarrow{\Delta}$ steam / vapour

   (solid) (liquid) (gas)

2. $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ $\boxed{\Delta s = +ve}$

3. Vapour $\xrightarrow{\text{liquid}}$ water $\xrightarrow{\text{liquid}}$ ice $\boxed{\Delta S = -ve}$

   (gas) (liquid) (solid)

❖ **The entropy of the universe is always increasing.** $\boxed{\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}}$

- ➢ For a spontaneous reaction, $\boxed{\Delta S = +ve}$
- ➢ For a non – spontaneous reaction, $\boxed{\Delta S = -ve}$
- ➢ A + equilibrium, $\boxed{\Delta S = 0}$

- For a reversible reaction, $\boxed{\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0}$ ....(i)
- For an irreversible reaction, $\boxed{\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0}$ ....(ii)

$\Rightarrow$ Now combining, $\boxed{\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0}$

e,g. $2H_{2(g)} + O_{2(g)} \xrightarrow{\text{electricity}} 2H_2O \rightarrow$ spontaneous reaction (required initiation)

$2H_2O \rightarrow 2H_2(g) + O_2(g)$

LECTURE 07

Gibb's Free energy :

- It is the total amount of energy available in a system under a given setup condition that can be put into useful work.

$\boxed{G = H - TS}$ (Where G = Gibb's free energy, H – Enthalpy, T = Absolute temperature, S = entropy)

So, we have,

$G_1 = H_1 - TS_1$ ....(i)

$G_2 = H_2 - TS_2$ ....(ii)

So, $G_2 - G_1 = H_2 - TS_2 - H_1 + TS_1$

$\Rightarrow \Delta G = (H_2 - H_1) - T(S_2 - S_1)$

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

$\Rightarrow$ Relationship between ΔG & ΔS :

At equilibrium, $\Delta G = 0$

$\Rightarrow \Delta H = T\Delta S$

For spontaneous reactions, $\Delta G = -ve$

For non spontaneous reaction $\Delta G = +ve$

At equilibrium, $\Delta G = 0$

$$\Rightarrow \boxed{\begin{aligned}\Delta_r G^0 &= -RT\ln k \\ &= -2.303\, RT \log K\end{aligned}}$$

1. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)} \Delta S = ?$

   So, $\boxed{\Delta S = -ve}$

2. $PCl_{5(g)} \rightarrow PCl_{3(g)} + Cl_{2(g)}$

   $\boxed{\Delta S = +ve}$

3. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O(g)$

   $\boxed{\Delta S = -ve}$

4. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

   $\boxed{\Delta S = -ve}$

❖ **Characteristics of Gibb's free energy :**

(i) It is a state function.

(ii) It is an extensive property

(iii) It has exact differential.

(iv) Its absolute value can not be measured accurately.

(v) Only the differential value can be calculated.

We know, $\boxed{G = H - TS}$

$G_1 = H_1 - TS_1$ ....(i)

$G_2 = H_2 - TS_2$ ....(ii)

Subtracting equation 1 from 2 , we get

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

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

$\Delta G = -ve$ (spontaneous) → direct process.

$\Delta G = +ve$ (non-spontaneous) → indirect process

$\Delta G = 0$ (equilibrium)

❖ **Relationship between standard Gibb's free energy change for a chemical reaction :**

$$\boxed{\begin{aligned}\Delta_r G^0 &= -RT\ LnK \\ &= -2.303RT\log K\end{aligned}}$$ [Where k is equilibrium constant]

Questions

01. When there is no exchange of matter from system to surrounding or viceverse.
02. When there is exchange of heat energy and matter from system to surrounding of vice-versa.
03. How ΔS vary with ΔH ?
04. How ΔG vary with ΔS ?

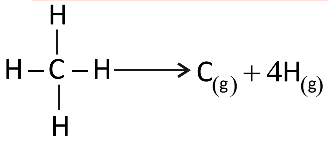
❖ **Entropy of atomisation (ΔaH) :**

- The enthalpy change during convertion of one mole of a molecule into its atom.

Eg. $H_2(g) \xrightarrow{\Delta_a H} 2H(g)$

$Cl_2(g) \xrightarrow{\Delta aH} 2Cl(g)$

❖ **Bond Enthalpy :**



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

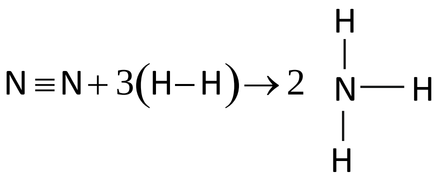
01. **Calculate the bond enthalpy of above reaction. Given the fond enthalpy of C – H = 94.5 KJ/mole.**

So, bond enthalpy = 4(94.5) KJ/mole – O = 378 KJ/mole.

- It is the average amount of energy, required per mole to break similar kind of bond in a molecule two its elementary form of constituent atom.
- Bond enthalpy of a chemical reaction.

$= \boxed{\sum \Delta_r H - \sum \Delta_P^H}$

02. $N_2 + 3H_2 \rightarrow 2NH_3$

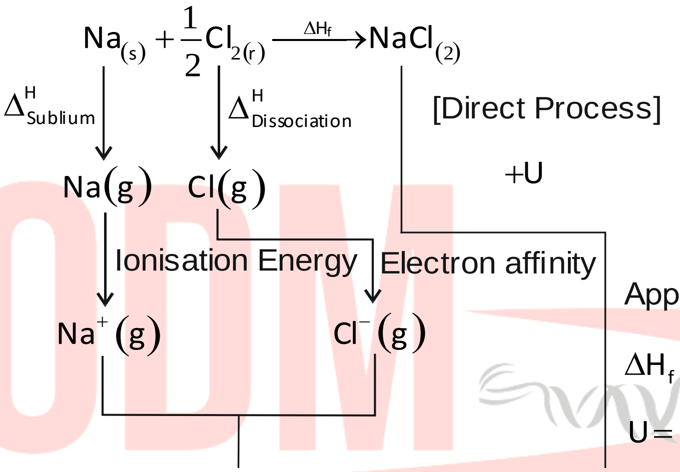


$$N \equiv N + 3(H-H) \rightarrow 2\,NH_3$$

Bond enthalpy of the reaction.

$$\sum \Delta_r H - \sum \Delta_p H$$

Born – Haber Cycle :



Applying Hess's law

$$\Delta H_f - \Delta H_{sub} + \Delta H_{0.135} + I.E + E.A. + U$$

$$U = \Delta H_f - (\Delta H_{sub} + \Delta H_{diss} + I.E. + I.A)$$