8. THERMODYNAMICS

SYNOPSIS: Introduction and Concepts :

- **THERMODYNAMICS:-** The subject dealing with Quantitative relation between heat energy and other forms of energy in physico - Chemical processes.
- **CHEMICAL THERMODYNAMICS :** The branch of thermodynamics which deals with the study of process in which chemical energy is involved is called chemical thermodynamics.
- These results are formulated in to four law's namely Zero, First, second and third laws of thermodynamics.
- There are three laws of Thermodynamics.
- These laws are based on experimental facts but not on the theoritical facts.
- Thermodynamics deals heat changes occuring between system and surroundings.
- Thermodynamics helps us to predict whether a particular chemical reactions occur on its own (or) not.
- **LIMITATIONS OF THERMODYNAMICS**
- Thermodynamics predicts the energy transformations and feasibility of a process.
- These laws donot give any idea about the rates of the processes.
- **TYPES OF SYSTEM:**
- **THE TERMS USED IN THERMODYNAMICS.**
- **SYSTEM**:- A small part of universe that is under thermodynamic study at that instant. It is any part of universe that is under thermodynamic study at that instant.
- It is a group of substances required for the conduct of an experiment.
- Ex : 1) A crystal (for a crystallographer)
- A physical process (for a physicist)
- Chemical reaction (for a chemist)
- **SURROUNDINGS** :- The remaining part of the universe.
- **Universe = system + surroundings**
- Systems are classified on the basis of their interaction with the surroundings as follows:

o **OPEN SYSTEM** :- The system where matter and energy are exchanged with surroundings.

- Boundary is not sealed and not insulated
- Eg. All living beings, A cup containg water.

o **CLOSED SYSTEM** :- The system where only the energy but not the matter is exchanged with the surroundings.

- Boundary is sealed but not insulated
- Eg. A closed steel cantainer having hot water.

o **ISOLATED SYSTEM**:- The system which does not exchange either the matter or energy with the surroudnings.

- Boundary is sealed and insulated
- Eg. A perfectly insulated, closed flask containing water.

- **THERMODYNAMICS PROPERTIES:**
- **STATE OF A SYSTEM**:- The system is said to be in a certain state, when it's macroscopic properties have definite values. It is defined interms of its state functions such as P,V,T etc.
- If any one of the state functions is changed, the state of that system is said to be changed.
- **EXTENISVE PROPERTY** :- It is the property of a substance that depends on its mass.
- Eg. Volume of a gas, Internal energy, Enthalpy, entropy, heat capacity, Gibbs energy, heat content etc.
- **INTENSIVE PROPERTY** :- It is the property of a substance that does not depend on its mass.
- Eg. Density, molar properties (such as molar volume molar entropy,molar heat capacity) surface tension, viscocity, specific heat, refractive index, pressure,temperature, boiling point,freezing point,vapour pressure.

- **WORK, HEAT AND ENERGY**
- These are important thermodyanamically useful concepts.
- There are algebraic quantities hence these can be positive (or) negative.
- **(MECHANICALWORK(W)** :- Work is said to be done when an unbalanced force causes some displacement in its own direction.
- The displacement of an object through a distance $'dx'$ against a force (F) is called work
- $W = F \times dx$

- This is measured in Joules (J), Kilo Joules (KJ), erg., Cal., etc.
- It is calculated as the product of external pressure and change in Volume

o $W = -(P\ V)$; $(V = V_{final} - V_{initial})$;

- 'W' is +ve when work is done on the system.
- 'W' is -ve when work is done by the system
- Work is a path function.
- 1 Joul = 0.2390 cal;
- 1 cal = 4.18 J
- 1 lit. atm = 101.3J= 1.013 x 10^9 erg = 24.2 cal.
- **Heat (Q)** :- It is the form of energy which flows between a system and surroundings by virtue of temperature difference.
- **Calorie** :- The heat required to raise the temperature of 1 gram of water by 1^oC is known as calorie.
- SI unit Joule.

- **ENERGY :**
- It is defined as the capacity to do work
- The property that is obtained through work or property that can be converted into work is known as **energy**
- Generally energy is two types (a) potential energy (b) kinetic energy.
- The unit of measurement of work and energy is the same (J or Cal or ergs)
- The energy , associated with a body or a system by virture of it position or state is potential energy
- Ex : Water stored at an elevated place
- Potential energy = mgx
- The energy , associated with a body or a system of mass 'm', moving with a velocity 'v' is known as kinetic energy
- Ex : Electron moving in an atom kinetic energy (KE) = 1/2 mv^2
- **STATE FUNCTIONS:**
- **STATE FUNCTION (OR) STATE VARIABLE**:- It is the property of a substance that depends on the state of that substance but not on the path of the system.
- State functions depends only on the initial and final states of the system.
- If 'z' is a state function, then it can be represented as $z = \int (P, T)$
- Z may be energy, volume, ethalphy etc.
- Eg. Internal energy, Enthalpy, Entropy, Gibb's energy, Temperature, Pressure, volume etc.
- **PATH FUNCTION** :- The property of a substance that depends on the path i.e how that substance is derived.
- Eg. work, heat.

- **FIRST LAW OF THERMODYAMICS :-**
- It was proposed by Robert Mayer, Helmholtz.
- It is another form of "law of conservation of energy".

- It can be stated as energy is neither created nor destroyed but it may be transformed from one form to another form.

- (or)

- "The energy of an isolated system is constant whatever changes take place in it"
- (or)

- "It is impossible to construct a perpetual motion machine of 1st kind that can work without consuming any form of energy"

- (or)
- "The net energy change in a closed system is equal to heat absorbed plus the work done by the system"
- The mathematical form of first law is
- $\Delta E = \Delta Q + W$ (or)
- according to IUPAC $q = dE + W$
- ΔE = Change in Internal energy ;
- ΔQ = heat gained or lost by the system;
- W = Work done by the system (or) on the system.
- For absorption of heat 'Q' is +ve and for release 'Q' is -ve
- When work is done on the system 'W' is +ve.
- When wrok is done by the system 'W' is -ve.

- **INTERNAL ENERGY (E (OR) U)** :- It is the sum of all types of potential and kinetic energies of constituent particles of a given substance at given temperature
- It is an extensive property and a state function.
- It is impossible to determine the absolute value of 'E' of a substance.
- But the change of Internal energy of a system
- (ΔE) can be determined.
- ΔE = heat absorbed (or) released in a process at constant volume and temperature
- ΔE =
- ($\Delta E = E_{final} - E_{initial}$)
- ΔE of a chemical reaction is determined in a Bomb calori meter.
- • For any chemical reaction $\Delta E = E_P - E_R$
- E_P = Total internal energy of the products
- E_R = Total internal energy of the reactants
- For any exothermic reaction
- $E_P < E_R$
- (ii) ΔE is negative
- For any endothermic reaction
- $E_P > E_R$
- ΔE is positive
- **ENTHALPY (H)** ;- The total heat content of a system at constant pressure is called it's enthalpy $\Delta H = Q_P$.
- It is a state function and an extensive property.
- It is calculated as the sum of internal energy and the product of pressure and volume.

- $\Delta H = E+PV$
- It is impossible to determine the absolute value of enthalpy.
- ΔH of a process can be calculated as
- $\Delta H = E + W$
- $= \Delta E + P \Delta V$
- **RELATION BETWEEN ΔH & ΔE:**
- • For any chemical reaction, at any constant temperature $\Delta H = \Delta E + \Delta n\ RT$
- T = absolute temperature of the reaction
- R = Universal gas constant
- $\Delta n = n_2 - n_1$
- n_2 = total number of moles of gaseous products
- n_1 = total number of moles of gaseous reactants
- $= \Delta E + \Delta nRT$

- Δn = no.of gaseous moles of products-
- no.of geseous moles of reactants.
- For any process which does not involve gases
- $\Delta H = \Delta E$
- **HEAT CAPACITY AND SPECIFIC HEAT :**
- . Heat capacity (C) of a substance in the amount of heat required to raise its temperature through one degree
- . Heat capacity is the ratio of heat absorbed by a system to the resulting increase in temperature
- $C = \frac{q}{dT}$
- q = heat absorbed by the system
- dT = rise in temperature
- . For gases, heat capacity is of two types -Heat capacity at constant volume (C_V) and heat capacity at constant pressure (C_P).
- . Heat capacity at constant volume (C_V) gives the measure of the change of internal energy (E) of a system with temperature
- $C_V = \left[\frac{\partial E}{\partial T}\right]_v = \frac{q_v}{dT}$
- . Heat capacity at constant pressure (C_P) gives the measure of the change of enthalpy (H) of a system with temperature
- $C_P = \left[\frac{\partial H}{\partial T}\right]_p = \frac{q_p}{dT}$
    - **RELATION BETWEEN C_p AND C_V FOR AN IDEAL GAS :**

- $C_p - C_v = R$
- $\frac{C_P}{C_V} = \gamma$
- Sepcific heat is the heat required to raise the
- temperature of one gram of a substance through 1^0C.
- Molar heat capacity or molar heat = Specific heat X molecular weight of the substance.
- Molar heat capacity at constant pressure C_p

$$C_P = \frac{q_P}{dT} = \frac{dH}{dT} = \left(\frac{\partial H}{\partial T}\right)_P$$

- Also, it is evident that $C_P = C_P \times M$ $C_V = C_V \times M$ C_p and C_V are specific heats at constant pressure and volume respectively and M is molecular weight of gas.

$$C_P - C_V = R$$

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

- **SPECIFIC HEAT CAPACITY (C) :**
- The quantity of heat required to raise the temperature of 1 gram of substance through 1k (or 1^0C)
- specific heat capacity $(C) = \frac{Heat\ capacity}{Mass} = \frac{C}{M}$

$C = \frac{q}{m\Delta T}$ (or) $q = C \times m \times \Delta T$

- Units of "C" $Jg^{-1}K^{-1}$ (or) $Jg^{-1}\left({}^0C^{-1}\right)$.
- The specific heat capacity (C) and molar heat capacity as (C_m) of the substance are related

$C \times molar\ mass = C_m$

- **EXOTHERMIC AND ENDOTHERMIC REACTIONS:**

EXOTHERMIC REACTION.

- A chemical reaction, which occurs with the evolution of heat, is known as **exothermic reaction.**

Eg : 1. $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} + 92$ K J

2. $C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)} + 393.5$ K J

- In exothermic reactions enthalpy of products $\left(H_p\right)$ is less than Enthalpy of the reactants $\left(H_R\right)$.

ENDOTHERMIC REACTION.

- A chemical reaction, which occurs with the absorption of heat from the surroundings, is known as **endothermic reaction.**

Eg : 1.$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$-180.8 K J

2.$C_{graphite} + 2S_{(g)} \rightarrow CS_{2\ (g)}$-91.9 KJ

- In endothermic reactions enthalpy of products is greater than enthalpy of the reactants.

$H_P > H_R$

$\Delta H = H_P - H_R$

$\Delta H = +ve$

- If the reaction occurs without any change in volume,
- Δ n = 0
- Δ H = Δ E
- If the reaction occurs with decrease in volume.
- Δn is negative
- ΔH < ΔE
- • If the reaction occurs with increase in volume.
- Δn is positive
- ΔH > ΔE
- **THE STANDARD CONDITIONS FOR A CHEMICAL REACTION ARE:**
- • temperature = 25^{o}C = 298^{o}A
- • Pressure = 1 atmosphere = 760 mm of Hg
- • The physical state of a substance under standard conditions (t = 25^{o}C, P = 1 atm) is known as standard physical state.
- **MEASUREMENT OF ΔE AND ΔH OF CHEMICAL REACTIONS:**
- ΔE is determined at constant volume and is determined at constant pressure.
- ΔH The technique of measurement heats of reactions is called calorimetry
- The apparatus used is called calorimeter.
- Water is the calorimetric liquid.
- Depending on the types of chemical reactions under study, two types of calorimeters are used.
- The first type is used in combustion reactions.
- The second type is used in the other types of reactions such as dissolution of solid in water and neutralization reaction
- **First type (for combustion reaction)**
- This type of calorimeter is known as bomb calorimeter
- This bomb is made of steel coated inside with platinum or gold or some other non - oxidisable material.
- A known weight of combustible substance is ignited by passing electric current through the platinum wire. The substance undergoes combustion and the heat liberated incerases the temperature of water in the calorimeter. The rise in temperature is measured accurately using a sensitive thermometer (Beckmann thermometer)

- The heat capacity of the calorimeter is determned using a known weight of benzoic acid prior to the main experiment.
- The heat of combustion of benzoic acid is - 3226 KJ / mole.
- Calculations: Let '' be the rise in temperature of water in the calorimeter after complete combustion of the experimental substance. The weight ofthe substance is 'm' gms. The molecular weight is 'M'. The heat capacity of (the calorimeter + water) is ' Z'
- The heat of combustion = $Z \times \theta \times \frac{M}{m}(cals)$
- In athe above experiment, the volume is constant. Hence heat of combustion is at constant volume (q_v) . q_v is converted into q_p using the equation $q_p = q_v + \Delta nRT$
- Δn = change in the number of gas molecules in the combustion reaction.
- **SECOND TYPE OF CALORIMETER**
- It is used for non combustion reactions such as solutions of Salt (or) organic compound in water (or) neutralisation reactions.
- This calorimeter contains two beakers one placed inside the other one. In between two beakers non-heat conducting material is placed.
- Dewar flask also can be used as calorimeter
- Water equivalent (W) ofthe calorimeter together with the stirrer and the thermometer is measured first .
- For this water at higher temperature ($t_2{}^0C$) of known mass (m_2) and water at lower temperature ($t_1{}^0C$) and mass (m_1) are used. These two are mixed in the calorimeter and the resultant temperature ($t_3{}^0C$) is noted.

$$W = \left[\frac{m_2 (t_2 - t_3)}{(t_3 - t_1)} - m_1 \right]$$

- Heat liberated = (W+ volume of reaction mixture) rise in temperature

ENTHALPY OF BOND DISSSOCIATION:

BOND DISSOCIATION ENERGY

- The amount of energy required to break 1 mole of a particular bond in a given compound and to separate the resulting gaseous atoms or ions or radicals from one another is bond dissociation energy.

$$H_2 \rightarrow 2H_{(g)} \quad \Delta H^0 = +435.9\, KJ\, mol^{-1}$$

- The bond dissociation energy in polyatomic molecules will be only average value, because in each step of dissociation different fragments are involved.

$$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)} \quad \Delta H^0 = 427.0KJ$$

$$CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)} \quad \Delta H^0 = 418.4KJ$$

$$CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)} \ \Delta H^0 = 460.2 KJ$$
$$CH_{(g)} \rightarrow C_{(g)} + H_{(g)} \ \Delta H^0 = 343.1 \ KJ$$

$$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)} \ \Delta H^0 = 1648.7 \ KJ$$

- $C-H$ bond dissociation energy = $\frac{1648.7}{4} = 412.2 KJ$
- **HEAT OF REACTION:**
- The quantity of heat liberated or absorbed at constant temperature when the reactants undergo a complete transformation into the products as per the stoichiometric equation is called **heat of reaction.**
- The enthalpy change of a chemical reaction is given by the symbol $\Delta_r H$
- $\Delta_r H$ =(sum of enthalpies of products) - (sum of enthalpies of reactants)
- $\Delta_r H$ = $\sum$ aiH products - $\sum$ biH reactants
- ai & bi are the stoichiometric coefficients.

- **HEAT OF COMBUSTION (ENTHALPY OF COMBUSTION):**
- The quantity of heat evolved when one mole of a substance burns completely in excess of oxygen at a given temperature and constant volume is called the heat of combustion of the substance.
- The heat of combustion is always negative.
- The heat of combustion of graphite is 393.5 kJ/mole. The thermo chemical equation for the combustion of one mole of graphite is
- $C_{(gra)} + O_{2(g)} \rightarrow CO_{2\,(g)}$; ΔH = -393.5 kJ

- **HEAT OF NEUTRALIZATION**
- **(ENTHALPY OF NEUTRALIZATION):**
- The quantity of heat evolved, when one gram equivalent of a base is completely neutralized by one gram equivalent of an acid in aqueous solutions, is known as the heat of neutralization.

  or
- The heat evolved, when 1 mole of H^+ ions react with 1 mole of OH^- ions in aqueous solutions to form one mole of water, is known as heat of neutralization.

  $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$; ΔH = -57.3 kJ
- The neutralization process results in the formation of salt and water.
- The maximum value of heat of neutralization is 57.3 kJ (or) 13.7 k cals.
- The heat of neutralization is maximum, when a strong base is neutralized by a strong acid.

- The heat of neutralization is minimum when a weak base is neutralized by a weak acid.

- Some examples for the neutralization reactions
- $HCl + NaOH \rightarrow NaCl + H_2O$; ΔH = -57.3 kJ
- $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$;
- ΔH = -55.22 kJ
- $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$;
- $\Delta H = -51.46$ kJ
- $CH_3COOH+NH_4OH \rightarrow CH_3COONH_4+H_2O$;

  ΔH = -49.3kJ

- If the acid or base or both are weak, the heat of neutralization is less than 57.3 kJ or 13.7 KCal
- The difference between 57.3 kJ and actual heat of neutralization is equal to the heat of ionization of weak acid or weak base (or) both, involved in the neutralization reaction.
- Ex : The heat of neutralization of NaOH with HCl is 57.3 kJ and with CH_3COOH is 55.22 kJ. The heat of ionization of CH_3COOH is +2.08 kJ.
- **HEAT OF FORMATION (ENTHALPY OF FORMATION):**
- The amount of heat evolved or absorbed when one mole of compound formed from it's constituent elements at constant temeprature is called heat of formation.
- The amount of heat energy released or absorbed, when one mole of a compound is formed in its standard physical state by the combination of elements taken in their standard physical states, is known as the **standard heat of formation** of the compound.
- The standard heat of formation of the compound is represented as ΔH_f^0 .
- The standard heat of formation of the compound may be positive or negative.
- Eg : Compound ΔH_f^0 in kJ/mol
  - $CO_{2\,(g)}$ = -393.5
  - $CO_{(g)}$ = -110.5
  - $NO_{(g)}$ = + 90.4
  - $NO_{2\,(g)}$ = + 33.85
- If the standard heat of formation is negative, the compound is called exothermic compound.
- The enthalpy of a compound is equal to its standard heat of formation.
- The enthalpy of a compound may be positive (or) negative.
- Exothermic compounds are thermodynamically more stable than endothermic compounds.
- **ENTHALPY OF ATOMIZATION**
- The heat required to dissociate one mole of a simple molecule in the gaseous state into its constituent atoms is called enthalpy of atomization.

- This is an endothermic process.

$H_{2(g)} \rightarrow 2H_{(g)}$; $\Delta H = 43.51 KJ$

$O_{2(g)} \rightarrow 2O_{(g)}$; $\Delta H = 489.5\, KJ$

$N_{2(g)} \rightarrow 2N_{(g)}$; $\Delta H = 937.4 KJ$

ENTHALPY OF SUBLIMATION

- some substances in the solid state at room temperature are converted into the gaseous state on heating. This process is known as sublimation are :

$Solid \xrightarrow{\Delta} Gas$

Ex :1) $Solid\ I_2 \xrightarrow{\Delta} I_2 vapour$

2) $Naphthalene_{(s)} \xrightarrow{\Delta} Naphthalene_{(g)}$

- This type of change is possible if only, If the pressure at which heating is carried out is much below the triple point pressure of the compound subliming.
- This process is an endothermic process $\left(\Delta H = +ve\right)$
- The amount of heat required to convert one mole of a simple substance in the solid state into the gaseous state without decomposition of the substance is called enthlpy of suplimation.
- solid CO_2 or “dry ice” sublimes at 195K with

$\Delta_{sub} H^{\theta} = -25.2 K.Jmol^{-1}$

$\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H$

- All these phase changes occur on change of temperature at atmospheric pressure.
- Solid - Liquid (fusion or melting)
- Liquid - Gas (Vapourization)
- Liquid - Solid (Freezing)
- Solid - Gas (Sublimation)
- One crystalline form $\rightarrow$ Another crystalline form

Ex : $\alpha - sulphur \rightarrow \beta - sulphur$

- The heat change involved inthe change of phase or physical state of one mole of compound at atmospheric pressure is called enthalpy of phase transition.

$C_{(s)} \rightarrow C_{(g)}$; $\Delta H = 1439.2\, KJ$

$S_{(monoclinic)} \rightarrow S_{(r\,hombic)}$; $\Delta H = -2.5\ KJ$

$S_{(r\,hombic)} \rightarrow S_{(monoclinic)}$; $\Delta H = +2.5\ KJ$

ENTHALPY OF IONIZATION IN AQUEOUS SOLUSTIONS

- The enthalpy change in the formation of an ion at unit activity (or concentration) from its elements in aqueous solution is enthalpy of ionization.

- The absolute value is not possible. Therefore , the enthalpy of $H^+_{(aq)}$ at 298 K is taken as zero arbitrarily

  $1/2H_{2(g)} + aq \rightarrow H^+_{(aq)} + e^- \;\; ; \Delta H^0 = 0.0KJ$

  the enthalpy of formation of other ions are adetermined relative to this value of zero for $H^+_{(aq)}$
- For OH^- it is -228.51 KJ

ENTHALPY OF DILUTION

- The change of enthalpy when a solution containing one mole of a solute is diluted from one concentration to another is called enthalpy of dilution
- When a solution is so dilute that further dilution causes no noticeable heat change, the solution is said to be at infinite dilution.
- Ex : 1 mole of KCl dissolved in 20 moles of water absorbed 15.90 KJ of heat . When 1 mole of KCl is dissiolved in 200 moles of water, 18.58KJ of heat is absorbed.
- The heat of dilution of KCl is, therefore, given as $\Delta H_2 - \Delta H_1 = 18.58 - 15.90 = 2.68KJ$

THERMOCHEMICAL EQUATIONS

- The chemcial equations in which heat change accompanying a reaction is also numerically specified with proper sign by Δ H or Δ E by theside of the equation are known as thermochemical equations.
- In these equations, the physical states of the reactants and the products are also mentioned in the brackets by the symbols
- Allotropes will also be mentioned
- The enthalpy of an element in its standard physical state is fixed as zero (actually enthalpy cannot be determined).
- Gases having H = 0, are H_2, O_2, N_2, F_2, Cl_2, inert gases
- Liquids having H = 0 are Br_2, Hg, H_2O, C_2H_5OH
- Solids having H = 0, All metals, Iodine
- If the element exhibits allotropy, the enthalpy is fixed as zero for the most stable and most abundant allotrope of the element.
- The enthalpy is taken as zero for rhombic sulphur, graphite, white phosphorus etc.,

- **HESS LAW:**
- The heat energy released or absorbed in a process is same whether the process occurs in one step or in several steps. This is known as Hess law of constant heat summation.

- According to Hess law the heat energy released or absorbed in a process depends only on the initial state and final state but not on the path**,** in which the process occurs.

- Hess law is applicable to both physical and chemical changes.
- Hess law is an application of first law of thermodynamics or law of conservation of energy.

$\phi_1 = q_1 + q_2 + q_3$

- **Hess law can be used to determine**
- Heat formation of a intermediate compounds which are unstable and it cannot be isolated.
- Heat of combustion of a substance
- Heat of transition
- Lattice energy of ionic compounds
- **SPONTANEOUS PROCESS** : - A process is sait to be spontaneous if it occurs on its won without the intervention of any external agency if any kind.
- Ex : Flow of Heat from High temperature to lower temperature.
- Flow of water from high level to low level.
- Flow of gas from high pressure to low pressure.
- • Sponteneous (or) natural process are thermodynamically irreversible.
- **DRIVING FORCES FOR SPONTANEOUS PROCESSES:**
- Tendency of a system to achieve a state of minimum energy .
- Tendency of a system to achieve a state of maximum randomness (entropy).
- The above two tendencies are independent of each other i.e both may act in same or opposite directions in a process.
- **SECOND LAW OF THERMODYNAMICS** :-
- It is stated in various forms. Some of them are as follows:
- Heat cannot flow from a colder body to a hotter body on its own.
- Heat cannot be converted into work completely without causing some permanent changes in the system or in the surroundings.
- All spontaneous processes are thermodynamiclly irreversible and entropy of the system inereases.
- It is impossible to construct a machine working in cycles and transfers heat from a lower temperature region to a higher temperature region without intervension of an external agency (such an imaginery machine is called perpetual motion machine of second kind).

ENTROPY -

- **ENTROPY (S)** :- Entropy is a meassure of randomness (or) disorder of the particles of a system"
- It depends on the temperature, pressure of the state.
- It is more convenient to use change of entropy (S)
- mathematically:
- Entropy is a state function and an extensive property
- $\Delta S = \Delta S_{final} - \Delta S_{initial}$

$= \Delta S_{products} - \Delta S_{reactants}$ (for a chemical reaction)

- $S = \frac{q_{rev}}{T}$
- For a spontaneous process in an isolated system $\Delta S > 0$ i.e positive.
- When a system is non isolated the entropy changes of the surroundings also must be considered.
- Then $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$
- (for a spontaneous process) ® $\Delta S_{total} > 0$.
- When ΔS is +ve, the process is spontaneous.
- When ΔS is -ve, the process is non - spontaneous.
- When $\Delta S = 0$, the process is in equilibrium.
- The entropy of a system increases when it absorbs heat.
- ΔS is more +ve when the system absorbs heat at lower temp rather that at higher temp.
- Units of S and ΔS are $J.K^{-1}$, mol^{-1}
- At a given temp $S_{liquid} > S_{solid}$ and $S_{gas} > S_{liquid.}$
- **ENTROPY CHANGE IN EXOTHERMIC AND ENDOTHERMIC REACTIONS** :-
- In exothermic reactions heat released by the reaction increases the dissorder of the surroundings and overall entropy change is positive $(\Delta S = +ve)$.
- In endothermic reactions heat flows from the surroundings into the system. The entropy of the surroundings decreases and the system increases.
- Total entropy changes positive. The change is spontaneous.
- **ENTROPY CHANGE DURING PHASE TRANSFORMATION** :-
- **ENTROPY OF FUSION** :- It is the change in entropy when one mole of a solid changes to a liquid at its melting point $\Delta S_{fusion} = \frac{q_{rev}}{T}$.

  $$\Delta S = \frac{\Delta H_{fusion}}{melting\ point(K)}$$

- **ENTROPY OF VAPOURISATION**:- It is the change in entropy when one mole of a liquid changes to vapour at its boiling point.

  $$\Delta S_{vapourisation} = \frac{\Delta H_{vapourisation}}{Boiling\ point(K)}$$

- **ENTROPY OF SUBLIMATION**:- It is the change of entropy when one mole of solid changes into vapour at a particular temperature.
- $\Delta S_{sub} = S_{vapour} - S_{solid} = \frac{\Delta H_{sub}}{T}$

THIRD LAW OF THERMODYNAMICS :-

- This is also known as **NERNST HEAT THEOREM**.
- It was proposed by Max plank W.Richard & walter in different forms.

- "The entropy of a pure and perfectly erystalline substance is zero at the absolute zero temperature.(-273^{0}C)

  $S_{\lim T \to 0} = 0$
- Third law imposes a limitaion on entropy value but not leads to any new thermodyamic concept.
- Absolute entropy of a substance at a temperature T, $S_T = \int_0^T \frac{C_P}{T} dT$
- Accurate determination of energy $\left(S_T\right)$ requires that the heat capacity at constant pressure $\left(C_P\right)$ must be determined accurately.
- But $\left(C_P\right)$ cannot be measured at absolute zero $\left(-273^0 C\right)$ (or) around absolute zero C_V value at abolute zero is obtained by using the extra polating technique and the **"Debye equation"**.
- Debye equation $C_v = aT^3$
- a = Constant for a substance
- At the vicinity of absolute zero $C_p = C_v$
- Hence absolute value of 'S' can be calculated using C_v value.
- **CALCULATION OF ENTROPY IN CHEMICAL REACTIONS:**
- For the general reaction $PA + qB \rightarrow mC + nD$
- ΔS^0 is given by $\Delta S^0 = \left[mS_c^0 + nS_c^0 \right] - \left[pS_A^0 + qS_B^0 \right]$,
- ΔS^0 are molar entropies

  Eg:- For a reaction $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(l)}$

  $\Delta S^0 = S^0_{H_2O(l)} - \left[S^0_{H_2(g)} + \frac{1}{2} S^0_{O_2(g)} \right]$

- **GIBB'S ENERGY (or) GIBB'S FUNCTION (G)** :-
- $\Delta H = -ve$ may be a condition but not a necessary and sufficient conditions for the spontaneous nature of a reaction.
- $\Delta S = +ve$ is a condition but is not necessary and sufficient condition for the spontaneous nature of the reaction.
- Gibbs introduced another thermodynamic function which involved both enthapy (H) and entropy (s) functions. This is known as free enrgy functions (G) G is reffered as Gibbs energy (or) Gibbs function.
- **Mathematically:** G = H – TS

  $\Delta G_{system} = \Delta Hsystem - T\Delta S_{sys} + S.\Delta T_{sys}$ for isothermal changes

  $\left(T = const\right) \therefore \Delta G = \Delta H_{sys} - T\Delta S_{sys}$

  $\Delta G = \Delta H - \Delta TS$

  (Gibb's - Helmholtz equation)
- In a non - isolated system

$\Delta G_{system} = - T \Delta S_{total}$

- It is the ultimate driving force of a spontanous process
- Which is indicated by -ve value of ΔG.

  i.e
- If $\Delta G < 0$ i.e -ve, the process is spontaneas
- If $\Delta G > 0$ i.e +ve, the process is non spontaneas
- If $\Delta G = 0$, the process is in equilibrium state
- The units of 'G' are same as that of energy.
- ΔG^{θ} of a reaction can be calculated from the following equation.

- $\Delta_r G^{\theta} = \sum \Delta_f G^{\theta}(\text{products}) - \sum \Delta_f G^{\theta}$ (reactants)

  =[sum of standard energies of formation of products] -
- [sum of standard energies of formation of reactants]

ΔH	ΔS	ΔG	**Nature of reaction**
-	+	-	spontaneous at all temperatures
+	-	+	Non-spontaneous at all temperatures
-	-	-(at low'T')	spontaneous
-	-	+ (at high 'T')	Non - spontaneous
+	+	+ (at low 'T')	non - spontaneous
+	+	- (at high'T')	spontaneous