CHEMICAL THERMODYNAMICS AND ENERGETICS

Q.1) What is thermodynamics? Give its limitations or characteristics

Ans:Thermodynamics: A branch of science which deals with different forms of energy,the quantitative relationship between them and the energy changes that occurs in physical and chemical processes is called thermodynamics.

Characteristics or Limitations of 'Thermodynamics' :
a)It is applicable only to macroscopic system and not to microscopic system.

b)It does not take into consideration the time factor involved in any transformation process.

c) It predicts the **feasibility (direction)** of a chemical reaction but cannot state whether the process will   be fast or slow.

d)It does not take into account any theory of atom or molecule to explain the property of a system.

e)It does not explains the mechanism of the process taking place   thermodynamically.

Q.2) Explain the following terms

1)System: A part of the physical universe chosen to study the thermodynamic properties is called system.e.g A reaction mixture consisting of reactants and products a stoppered bottle is a system.

2)Surroundings: All other parts of the universe outside the system where the observations are made are called surroundings. E.g If the chemical reaction is carried out in a water bath, the the surroundings is the water bath.

3)Open system: A system that can of exchange matter as well as energy with its surroundings is called open system e.g., boiling water contained in a beaker can exchange matter (vapour) as well as energy in the form of heat with the surroundings.

4)Closed System: A system that can exchange energy only but not matter with the surroundings is called an closed system e.g. when hot water is enclosed in a sealed vessel, only heat energy escapes to the surroundings without changing the amount of water in the vessel. Thus it forms a closed system.

5)Isolated system: A system which cannot exchange either matter or energy with its surroundings forms an isolated system, e.g. a thermos flask containing a boiling liquid forms an isolated system. Here the total amount of energy remains constant.

e.g Hot tea or liquid kept in a thermos flask

**Q.3) Explain the properties of the system**

Ans: A system possess two properties

a)Extensive property: It is a property of the system whose magnitude depends upon the amount of matter present in the system. It is an additive property e.g. **mass, volume, surface area, work, energy, internal energy , enthalpy, entropy.**

b)Intensive property: It is a property of the system whose magnitude is independent of the amount of matter present in the system .It is not an additive property.e.g. **pressure**, **density**, **refractive index, temperature, surface tension,molar heat capacity.**.

4) Explain the term 'State function.'

Ans. Any property of a system whose value depends upon the current state of the system and is independent of the path followed to reach that state is called the state function.
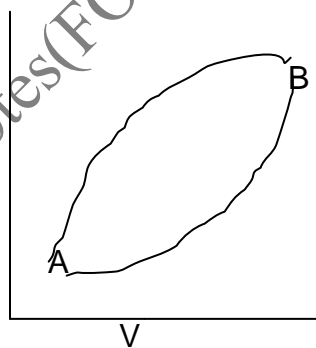
For example, in the accompanying figure, if P_1 and V_1 are the initial pressure and volume of the system at state A and if the system changes from state A to state B where the pressure and volume in state B are P_2 and V_2 respectively, then the change in pressure and change in volume are independent of the path followed. Hence pressure and volume are state functions. Other state functions include enthalpy, entropy, mass temperature etc.

Two important properties of state functions are as follows:

i) If the values to a few state functions are assigned then the values of all other properties are automatically fixed for example, Consider a system consisting of ideal gas.The ideal gas equation is PV=nRT.If the two properties such as pressure and temperature are fixed, then the third property volume gets automatically fixed as the number of moles and the value of R are constant.

ii) The change in any state function depends upon the initial and the final states of the system and not on how the change is accomplished.

5)'Work and heat are path functions.'Explain

Ans: Work as path function:

Consider a gaseous that undergoes a volume change from initial volume V_1 to final volume V_2 by three paths as shown below:
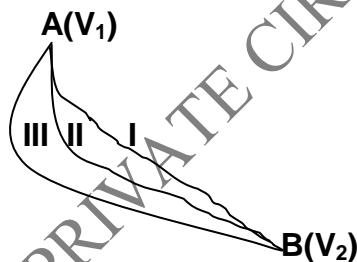
In path I the system is allowed to expand freely in vacuum from V_1 to V_2.Thw work done in this case is zero.

In path II the gas is allowed to expand isothermally against a constant external pressure .The work done in this case is given by

$$W = -p_{ext}.\Delta V = -p_{ext}.(V_2 - V_1)$$

In path III, the gas is allowed to undergo expansion from V1 to V2 isothermally and reversibly.The work obtained during this expansion is given by

$$W_{max} = -2.303nRT\log V_2/V_1$$

Thus in each path, the work done is different. The work depends upon the path chosen and hence it is a path function and not a state function.

b) **Heat as path function**:

Consider a gaseous system which undergoes a change from initial state A to final state B by two different paths as shown below:

PathI Adibatic

q=0

B

Path II Isothermal(q ≠ 0)

A
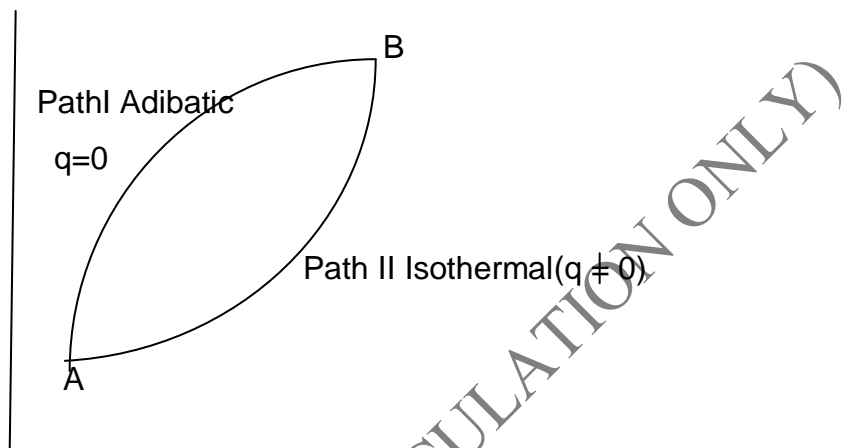
In **path I**, the system undergo an adiabatic change from A to B.There is no exchange of heat between the system and the surrounding i.e q = zero.

In **path II**, the the system changes from state A to state B isothermally.A quantity of heat q enters the system. i.e q ≠ 0.

Thus the initial and final state of the system are same but the amount of heat transferred is different for two paths .i.e **q** depends upon the path chosen hence it is a path function and not a state function.

6) Explain the following processes:

a) **Isothermal process** :The process in which temperature of the system remains constant throughout its transformation is called isothermal process.This is achieved by placing a system in constant temperature water bath i.e thermostat.For such a process, $\Delta T= 0$ and $\Delta U=0$

b) **Isobaric process**:The process in which pressure of the system remains constant throughout the change is called isobaric process.Most of the chemical reactions in the laboratory are carried ou in open vessels hence are oisobaric.similarly, the process of boiling and freezing of water are isobaric.In such a process, $\Delta P=0$

c)Isochoric process:A process during which the volume of the system remains constant is called isochoric process. A chemical reaction carried out in a close container is isochoric.For such a process, $\Delta V=0$

d) **Adiabatic process** : It is a process in which no heat exchange takes place between the system and the surroundings in any step of the process. The adiabatic conditions are achieved by carrying out the process in a thermos flask.For such a process, q = 0 ,$\Delta H = 0$.But ΔE is not equal to zero.

7) Explain the term reversible process

Reversible process: It is an imaginary or hypothetical process in which the driving force is only infinitesimally greater than the opposing force and the direction of which can be reversed by an infinitesimal increase in opposing force.

Consider a gas enclosed in a cylinder fitted with a weightless and frictionless piston.If the pressure of the gas is equal to external pressure acting on the piston, then the system is said to be in mechanical equilibrium.If the external pressure is decreased by an infinitesimal amount, then the piston will move up slowly and the gas will expand.However, if the external pressure is increased by and infinitesimal amount over the pressure P of the gas, then the piston moves inwards.Thus when a system is in mechanical equilibrium with the surroundings, ,an infinitesimal change in the conditions can cause the process to occur in opposite directions.The process is therefore thermodynamically reversible process.

8) Give the salient features of reversible process
Ans: The salient features of a reversible process are as follows:
 i) It is a very slow process and involves large number of steps.
 ii) The driving and the opposing forces differ by an infinitesimal amount.
 iii) There exist equilibrium between the system and surroundings in each and every step.
 iv) Maximum work is obtained from the reversible process.

 v) The process can be reversed at any point by making an infinitesimal change in conditions of the process.

9) Explain the concept of maximum work.

Ans.Definition of maximum work : The work done by an **ideal gas** during **isothermal expansion** under strictly **reversible conditions** is called maximum work .

Explanation for maximum work :Thermodynamically, a reversible process proceeds infinitesimally slowly and exhibit a state of equilibrium of system and surroundings at each and every stage . In such a process, the opposing pressure is infinitesimally smaller than the pressure of the gas. The direction of the process can be reversed by increasing the opposing force infinitesimally.

Assume that an ideal gas is enclosed in a cylinder fitted with weightless and frictionless piston .When the gas expands in vacuum , the external pressure is zero. Therefore work done by the gas is zero

i.e. $$W = -p_{ext.}.\Delta V = 0 \times \Delta V = 0 .$$

If the **external pressure** on the gas is slowly increased from zero, more and more work will be done by the gas to overcome this opposing pressure . If the external pressure (Pext.) becomes equal to the pressure (P) of the gas, then there will be no change in the volume of the gas as the opposing forces will be balancing each other

Therefore, it is possible to get the maximum work done by the system only when the external pressure is infinitesimally smaller in magnitude than the pressure of the gas itself.

Hence maximum work is the work obtainable from a system when the ideal gas expands isothermally and reversibly.

The maximum work done by an ideal gas during isothermal and reversible expansion is given by the expression

$$W_{max} = - 2.303 \ n \ R \ T \ log_{10} V_2/V_1$$

10)What are the conditions for maximum work obtainable from the system?

Ans: Maximum work is obtainable from a system under the following conditions

i) The process should be thermodynamically reversible.

ii) The driving and the opposing forces involved in the process should differ by an infinitesimal amount.

iii) The change occurring in the system should involve infinite number of steps.

iv) The system and its surroundings should be in mechanical equilibrium.

11) Distinguish between

A) Reversible process and irreversible process

Ans:

ReversibleProcess	IrreversibleProcess
1)It is an imaginary or hypothetical process	**1)** It is a naturally occurring process .
2)The driving and opposing forces differ by an infinitesimal amount	**2)** There exist a large difference in the magnitude of driving and opposing . forces
3) Equilibrium exists at each and every stage .	**3)** Equilibrium is reached at the end
4) It yields maximum work under under isothermal conditions.	**4)** It does not yield work under isothermal conditions.

B) Isothermal and Adiabatic process:

Ans:

Isothermal Process	Adiabatic process
1)The temperature of the system remains constant	**1)** The temperature of the system does increases or decreases.
2) System exchanges heat with the surroundings.	2) No exchange of heat from the system to the surroundings and vice versa.
3)Internal energy remains constant.	3) Internal energy increases or decreases
4) System is not thermally isolated from. the surroundings	**4)** System is thermally isolated. .

12)

A)Derive an expression for work done in an isothermal and irreversible process.

Ans. Assume that an **ideal gas** is enclosed in a cylinder fitted with a **weightless and frictionless piston**.   Let **A** be the area of cross section of the cylinder.Let the gas be allowed to expand isothermally against the external pressure(Pext.) from initial volume V_1 to final volume V_2. If **'dl'** is the small distance moved by the piston in the upward direction , then the work done during expansion is given by -

Work done = opposing Force x displacement

$$W = - f \times dl \qquad\qquad \text{------------ I}$$

The negative sign suggest that when the piston moves against the opposing force, the internal energy of the system doing the work decreases.The opposing force is the product of external pressure p_{ext} and area A of the cross section.

$$\therefore\ f\ = -p_{ext.}\ \times\ A$$

Substituting   f **= P x A** in equation **I** we get

$$W\ \ =\ -\ p_{ext.}\ \times A \times dl$$

But area x displacement i.e., A x dl = change in volume = dV = $V_2 - V_1$

$$\therefore W\ =\ -\ p_{ext.}\ dV$$

$$=\ -\ p_{ext.}(\ V_2\ --\ V_1)$$

During expansion, **Final volume > Initial volume**

i.e., $V_2 > V_1$.'. $\Delta V == +ve$ as well as W = -ve. .'.   Work done is   -ve   and is said to be done by the gas (i.e., system) on the surroundings.

During compression. **Final volume < Initial volume.i.e. $V_2 < V_1$** $\therefore \Delta V\ =$ +ve, hence W = P. ΔV =+ve.

Since work done is +ve, the work is said to be done by the surroundings on the system.

B)Derive an expression for work done by an ideal gas during isothermal and

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reversible expansion of an ideal gas.

Ans. Consider **'n'** moles of an ideal gas enclosed in a cylinder fitted with a **weightless and frictionless piston**.Let P be the pressure of the gas.The expansion is carried out **isothermally and reversibly(infinitesimally slowly)** in such a way that the external pressure **(p_{ext})** is infinitesimally smaller than the pressure P of the gas.
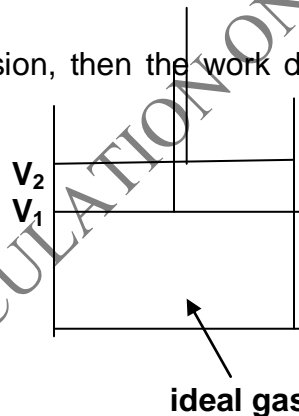
p_{ext} = (P -dP) where dP is infinitesimally small.

If a small change in volume dV is allowed during expansion, then the work done will also be small. This work done is given by

$dW = -p_{ext}.dP = -(P – dP). dV = -P.dV + dP. dV$

Since **dP** and **dV** are very small, the product
dP.dV will be negligible and can be neglected

$$dW = -P.dV$$

V_2
V_1

ideal gas

As the expansion is carried reversibly, there exist an equilibrium between system and surrounding at each and every stage.Therefore, there will be a series of **P.dV** terms with the pressure of the gas decreasing continuously and the volume increasing from **V_1** to **V_2** . Therefore total work done will be the sum of all these **P.dV** terms. This can be obtained mathematically by integration

$$\int dW = \int_{V_1}^{V_2} -P.dV$$

$$W_{max.} = \int_{V_1}^{V_2} -P.dV$$

For an ideal gas,

$$PV = nRT$$
$$V = nRT/P$$

$$\therefore W_{max} = - \int^{V_2} nRT/V .dV$$

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$$V_1$$

$$= -n.R.T(\ln V_2 - \ln V_1)$$

$$= -n.R.T.\ln V_2/V_1$$

By converting the natural log to the base 10, we get

$$\boxed{W_{max} = -2.303 \, n.R.T \log_{10} V_2/V_1}$$

During expansion, $V_2 > V_1$ ∴ W is negative.

During compression, $V_2 < V_1$ ∴ W is positive

At constant temperature, for an ideal gas we have,

$$P_1 . V_1 = P_2 . V_2 \text{ from } \textbf{Boyle's law}$$

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\boxed{W_{max} = -2.303 \, n.R.T \log_{10} P_1/P_2}$$

13) Write a short note on internal energy.
Ans.The total of all the possible kinds of energy associated with the matter in a system is called the internal energy (E) of the system.

Ans: Every substance has definite amount of energy stored in it. This is known as internal energy which may be partly kinetic and partly potential. The **kinetic part** is due to **translational, rotational** and **vibrational** motion of the molecules. As these motions are due to heat energy in the molecule, it is called thermal energy.

The **potential energy** is due to energy of the bonds within a molecule (E intramolecular or E_{intra}) and due to intermolecular forces (E intermolecular or E_{inter}).

Besides, energy required to keep neutrons and protons together in a nucleus,nuclear energy and energy associated with motion of electrons,i.e., electronic energy also accounts for internal energy.

$$U = U_{kinetic} + U_{potential} + U_{nuclear} + U_{electronic}$$

$$= (U_{translational} + U_{rotational} + U_{viibrational}) + (U_{intermolecular} + U_{intramolecular})$$

Internal energy is a state function. The absolute value of internal energy is difficult to calculate. Hence only the changes in internal energy are measured.

14)Discuss the various sources of internal energy

Ans: Internal energy is the total amount of different forms of energies stored in a substance. A substance is made up of large number of molecules. Molecules, in turn are formed by the union of two or more atoms of similar or dissimilar elements. When a substance undergoes a physical or a chemical change, energy is either evolved or absorbed. This energy change results due to the contribution of energy made by the molecules of the substance and energy due to atoms within the molecule.i.e., the total energy stored in a substance is the sum of potential and kinetic or (Thermal) energies.

Internal energy = potential energy   +   kinetic energy
(Bonding energy)   (Thermal energy)

I)**Bonding energy or Potential energy** :It is the energy which arises due to forces existing between molecules of a substance and from the interatomic attraction within the molecules. The former is termed as intermolecular energy and the latter is known as intramolecular energy. Therefore, bonding energy is the sum of intramole and intermole energy. It is sometimes called as internal energy. It is independent of external factors like temperature.

a) Intramole energy :This type of energy arises due to the interatomic attraction within a molecule. In a molecule, the atoms are linked by chemical bonds.

When a molecule is formed from its elements, energy is liberated. On the other hand, energy is absorbed when the molecules break up into atoms. **This energy released or absorbed during the breaking or formation of chemical bond is called intramole energy.**

b)Intermolecular energy:All substances in solid, liquid and gaseous state are made up of molecules. In solids and liquids, molecules attract each other due to weak **Van der waals** forces. In gaseous state, these forces are negligible. **The energy required to separate molecules from one another is called intermolecular energy.**

II)**Kinetic or Thermal Energy**: The energy which arises due to translational, rotational and vibrational motion of the molecules is called kinetic energy. It increases with increasing temperature. Therefore, it is also called as thermal energy. It is of three types :

a) **Translational energy**:The energy possessed by molecules both in liquid and gaseous state due to translational motion in a straight line path along the three coordinate axis is called translational energy. The molecules of gas are more free to move than the molecules of solid and liquid states.

b) **Rotational energy** : The energy that arises due to rotation of atoms of the molecules about an axis perpendicular to the line joining the two nuclei is called rotational energy. All diatomic and polyatomic molecules rotate about the axis perpendicular to the line joining the two nuclei. In solids, rotation does not take place and they possess only vibrational energy. In monoatomic gases like He, Ne, Ar, etc. only translational energy is present as the atom neither rotates nor vibrates.

c)**Vibrational energy** : The energy possessed by a molecule due to the vibrations of its atoms is called vibrational energy.

15).'**Internal energy is a state function.'Explain.**

Ans.Internal energy as state function: As internal energy of a substance depends upon its chemical nature which includes various indeterminant factors such as rotational, translational movement, attractive or repulsive forces between molecules etc; the absolute value of internal energy cannot be determined but change in internal energy can be calculated. Internal energy is therefore a state function because change in internal energy does not depend upon the path followed. This can be explained as follows.

Explanation: Consider a system which is subjected to a change of pressure volume

only. Let A & B be the initial and final states of the system with internal energies E_a & E_b associated with each state ,respectively.

Suppose the change of state is carried out from **A to B** by the system by absorbing some energy from the surroundings through **path I**.If ∆U is the change in internal energy,then

$$\Delta U = U_B - U_A$$

If the same change is brought about by another path **II** from B to A, then the change in internal energy would be given by

$$\Delta U^1 = U_B - U_A$$

If ∆U > ∆U¹, then surplus energy would be gained even when the system is brought back to the original state A by **path I** followed by **path II**. This mean that changing from path A to B , energy is created or obtained. But this is contradictory according to first law of thermodynamics

$$\Delta U = \Delta U^1$$

Thus we conclude that change in internal energy of a system, when a system changes from one state to another, depends upon the initial and final state is independent of the path followed.

16)Give the various statements of first law of thermodynamics or the law of conservation of energy.What is its corollary?

Ans.First law of thermodynamics:It is based on the principle of conservation of energy.The law is stated in number of ways.

a) The total internal energy of an isolated system is constant..

b)When one form of energy disappears, an exactly equivalent amount of energy of other form makes its appearance .

c) Energy can neither be created nor destroyed , but can be transformed from one form to another form in equivalent amounts.

d) The total quantity of energy of the universe is constant.

e) It is impossible for any machine to produce work without consuming energy.

   Such a machine is called perpetual machine .

Corollary of first law: Mechanical work and heat are mutually and completely

interconvertible

17) Give the limitations of first law of thermodynamics

Ans:i) It fails to explain the direction in which the physical and chemical processess

occurs spontaneously.
ii) It does not put any restriction on the direction of flow of heat.

iii) It is unable to predict the feasibility of a process in a particular direction.

iv) It does not clarify the extent of convertibility of one form of energy into other.**i.e.**it is unable to explain complete conversion of heat into work without leaving permanent changes on the system or surroundings.

18) State and explain zeroth law of thermodynamics

Ans When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

If the system A is in thermal equilibrium with a system C and with system B,then then B and c will be in thermal equilibrium with each other.
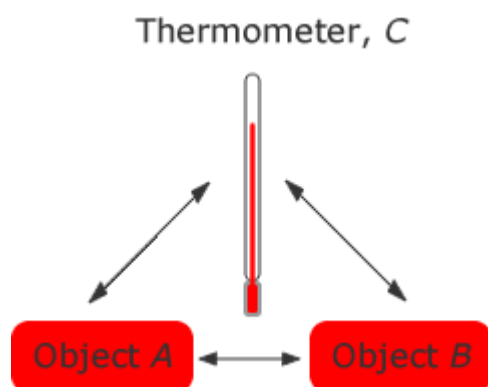
Thermal equilibrium: Two systems are said to be in thermal equilibrium if there is no net flow of heat between them when they are brought into thermal contact.

Temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature

Explanation

The zeroth law of thermodynamics is an observation. *When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.*

Consider three objects A, B and C as shown in the above figure. Object **C** and object **A** are in physical contact and in thermal equilibrium. Object B is also in thermal equilibrium with object A. There is initially no physical contact between object C and object B. But, if object B and object C are brought into contact, it is observed that they are in thermal equilibrium. This simple observation allows us to create a **thermometer**.Objects in thermodynamic equilibrium have the same temperature

19) Derive the mathematical expression for the first law of thermodynamics.
Ans: The internal energy of a system can be increased in two ways:

 1) by supplying heat to the system.

 2) by doing work on the system.

Consider a system with internal energy U_1 in the initial state **A**. Let the system absorb **q** joules of heat from the surroundings. As a result, the internal energy of the system will increase to $U_1 + q$

Therefore, Energy at initial state = $U_1 + q$

The heat energy absorbed is also utilized to do work of expansion..

If w is the work done on the system, then the internal energy will further increase and will become equal to $U_1 + q + W$. Let the final state of the system be B with internal energy U_2

According to first law of thermodynamics, as total energy of an isolated system remains constant, if

$$U_2 = E_1 + q + W$$

Therefore,
$$U_2 - U_1 = q + w$$

Therefore, | $\Delta U = q + W$ | ------------------I

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This is the mathematical expression of first law of thermodynamics.

In equation , **W** = work done on the system by the surroundings.
Δ**U** = Change in internal energy
Q = heat absorbed.

For infinitesimal change, equation I can be written as

$$dU = dq + dW$$

Mathematical statement of first law is as follows :

The change in internal energy of system (ΔE) brought about by the absorption of heat energy 'q" is equal to the sum of the amount of heat absorbed (q) and work done on the system (Here q >w)

20) Give an expression for first law of thermodynamics in the following Processes

 a) I**sobaric   b) Isothermal   c) Isochoric   d)Adiabatic**

Ans: The mathematical expression for first law of thermodynamics is given by

$$\Delta U = q + W$$

where q = heat absorbed by the system
Δ**U** = change in internal energy
w = work done on the system

a) Isobaric process: In isobaric process, pressure is constant. Therefore work done is - $P_{ext}.\Delta V$.Hence,

$$\Delta U = q_p - P_{ext.} \Delta V$$

b) Isothermal process: In isothermal process, $\Delta U = 0$.

$$q = -W \qquad ------------- II$$

Work done by the system is equal to the heat absorbed by the system.

Equation II suggest that for isothermal process,heat absorbed is entirely used for doing work on the surroundings or work done on the system by the surroundings results in release of heat by the system.

c) Isochoric process: In this process, $\Delta V = 0$, therefore P. $\Delta V = 0$

$$q_v = \Delta U$$

The above equation suggest that the change in internal energy of the system is due to heat transfer**.**

d) Adiabatic process: In this process, q =0 , therefore

$$\Delta U = W$$

The above equation suggest that the change in internal energy of the system is due to work done on it by the surroundings.

21) Explain the term 'enthalpy of the system.'
Ans:.It is a measure of total heat content of a system,i.e., the total heat content of a system at constant pressure is equivalent to **sum** of **internal energy** and **pressure-volume** energy is called enthalpy of the system.

Most of the chemical reactions are carried out at constant pressure ie at atmospheric pressure The heat changes accompanying these reactions at constant pressure are conveniently expressed by a new thermodynamic function called enthalpy

Mathematical definition of enthalpy: Enthalpy is mathematically defined by the expression

$$H = U + P.V$$

where   H = enthalpy of the system
        E = internal energy of the system
        P = Pressure of the system
        V = Volume of the system
Enthalpy is a state function: Internal energy (E), pressure P and volume V are all state functions. The value of H depends on E , P and V. Hence, it must also be a state function. Therefore, change in enthalpy ΔH only depends upon initial and final state and is independent of path followed.

22) Derive an expression for enthalpy change.
Ans:
    By definition, enthalpy of a system is given by

$$H = U + P.V$$

If **H_1** and **H_2** are the heat contents or enthalpies at the initial and final state respectively, then the change in enthalpy is given by

$$\Delta H = H_2 -- H_1$$

Substituting the value of H in the above equation, we get,

$$\Delta H = (U_2 + P_2.V_2) -- (U_1 + P_1.V_1)$$

$$= (U_2 - U_1) + (P_2.V_2 - P_1.V_1)$$

$$= \Delta U + \Delta(PV)$$

At constant pressure, $P_1 = P_2 = P$

$$\Delta H = (U_2 - U_1) + P.(V_2 - V_1)$$

i.e., $\Delta H = \Delta U + P.\Delta V$

23)Show that the heat absorbed at constant pressure is equal to the enthalpy change of the system.
Ans: From first law of thermodynamics,

$$\Delta U = q + w$$

If work done during the change is expansion work only, then
$$W = -p_{ext}.\Delta V$$

Therefore $\quad\quad\quad \Delta U = q - p_{ext}.\Delta V \quad\quad\quad\quad\quad$ ----------- I

Assuming that the pressure is same inside and outside, i.e the system is in mechanical equilibrium, $p_{ext} = P$, equation I can be written as

$$\Delta U = q_p - P.\Delta V \quad\quad\quad\quad\quad$$ ---------- II

where q_p is the heat absorbed at constant pressure.

On rearranging equation II, we get

$$q_p = \Delta U + P.\Delta V \quad\quad\quad\quad\quad$$ ------------III

By definition, enthalpy of a system is given by

$$H = U + P.V$$

If H_1 and H_2 are the heat contents or enthalpies at the initial and final state respectively, then the change in enthalpy is given by

$$\Delta H = H_2 - H_1$$

Substituting the value of H in the above equation, we get,

$$\Delta H = (U_2 + P_2.V_2) - (U_1 + P_1.V_1)$$
$$= (U_2 - U_1) + (P_2.V_2 - P_1.V_1)$$

At constant pressure, $P_1 = P_2 = P$
$$\Delta H = (U_2 - U_1) + P.(V_2 - V_1)$$

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$$\text{i.e.,} \quad \Delta H = \Delta U + P.\Delta V \quad \text{--------- IV}$$

From equation III and IV, we get

$$\Delta H = q_p$$

Thus the heat absorbed at constant pressure is equal to the enthalpy change of the system.

24) Show that the heat absorbed at constant volume is equal to the change in internal energy of the system.
Ans: From first law of thermodynamics,

$$\Delta U = q + W \quad \text{--------- I}$$

If work done during the change is expansion work only, then
$$W = - p_{ext}.\Delta V \quad \text{----------- II}$$

Assuming that the pressure is same inside and outside, i.e $p_{ext} = P$, equation II can be written as
$$W = - P.\Delta V$$

Therefore $\quad \Delta U = q_v - P.\Delta V \quad$ ----------- III

where q_v is the heat absorbed at constant volume.

At constant volume, $\Delta V = 0$ therefore $P.\Delta V = 0$

Therefore $\quad q_v = \Delta U$

i.e heat absorbed at constant volume is equal to the change in internal energy of the system.

25) Give the various statements of second law of thermodynamics.
 i) All naturally occurring processes are thermodynamically irreversible in nature.

 ii) All naturally occurring processes always tends to change spontaneously in a direction which will lead to equilibrium.

 iii) Heat cannot be completely converted into an equivalent amount of work without producing permanent changes either in the system or their surroundings.

 iv) A spontaneous process is always accompanied by an increase in total entropy **(**of the system and surroundings).

v) The spontaneous flow of heat is always unidirectional, from higher temperature

to lower temperature