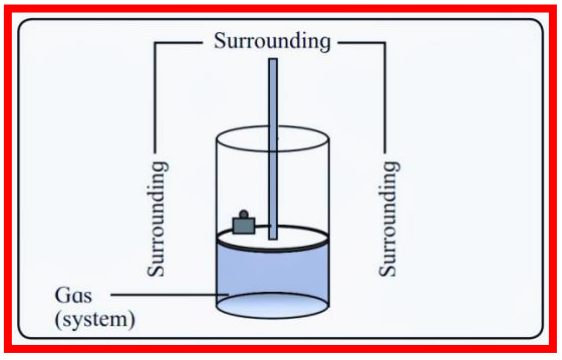
4. CHEMICAL THERMODYNAMICS

Introduction: You know transformation of liquid water into vapour, solid ice into liquid water or burning of carbon forming carbon dioxide, CO_2, are accompanied by a change in energy. In dry cell, the chemical energy is converted into electrical energy. On the other hand, in electroplating of metals electrical energy is converted into chemical energy. Thus it may be realized that the energy can be transformed from one form into another.

Define Thermodynamics

Thermodynamics is defined as the branch of science which deals with the study of interconversion of different forms of energy and the quantitative relationship between them taking place in physical and chemical processes.

Terms used in thermodynamics:-



System and surrounding concept: Consider a gas enclosed in a cylinder equipped with a movable piston as shown in the below Figure. Suppose we undertake study of change in volume of a gas and the amount of energy released or gained by a gas when the pressure is varied by putting certain mass on the piston. In this case, a gas under study is called the system.

Q.1 Define System:- A part of the universe under thermodynamic investigation is called the system.

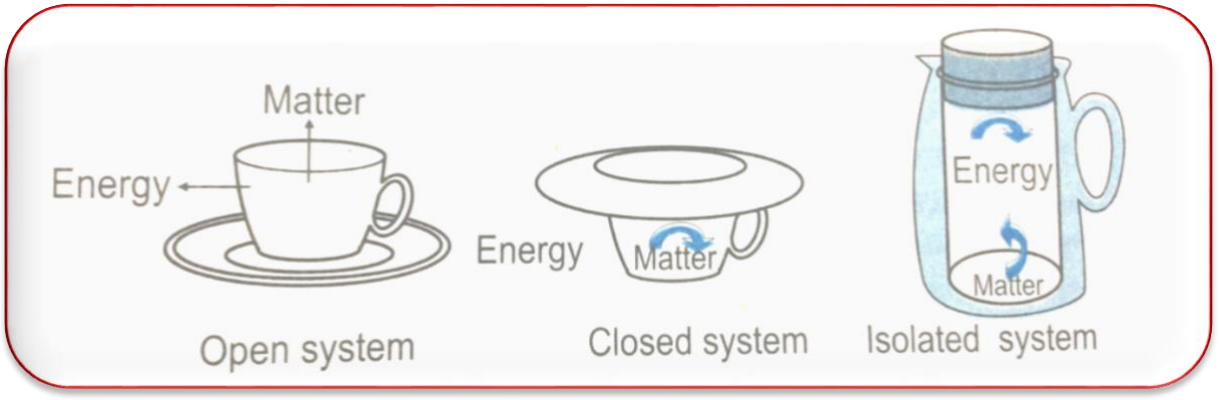
Q.2 Define Surrounding:- All other parts of the Universe outside the system such as cylinder, room and others, are surroundings.

Q.3 Define Boundary:- The wall or interface separating system from its surrounding is called as boundary.

The universe is made of system and surrounding.

SYSTEM + SURROUNDING = UNIVERSE

Q.4 TYPES OF SYSTEM:- [State and explian types of system with example]



(a) (b) (c)

Ans:- In thermodynamics there are three types of system:

i) open system ii) closed system iii) isolated system

i. Open system: The above figure (a) shows an open cup containing hot coffee placed in a room. You observe coffee cools down releasing heat to the surroundings. The water vapour from coffee simultaneously passes into the surroundings. Such a system (coffee) which exchanges both energy and matter with the surroundings is called an open system.

ii. Closed system: The above figure (b) shows a cup containing hot coffee is covered with a saucer. Coffee cools down by giving away heat to the surroundings. The water vapour from coffee now does not pass into surroundings. Such a system that exchanges energy and not the matter with the surroundings is called a closed system.

iii. Isolated system:- The above figure (c) shows a cup containing hot coffee is covered with a saucer is insulated from the surroundings. Coffee does not cool down. There is no escape of water vapour into the surroundings. Such a system that does not allow exchange of either or matter with the surroundings is an isolated system.

Q.5 PROPERTIES OF SYSTEM:- [Define properties of system and give examples]

➪ EXTENSIVE PROPERTY:- A property which depends on the amount of matter present in a system is called an extensive property.

Examples:- Mass, volume, internal energy, heat capacity, number of moles.

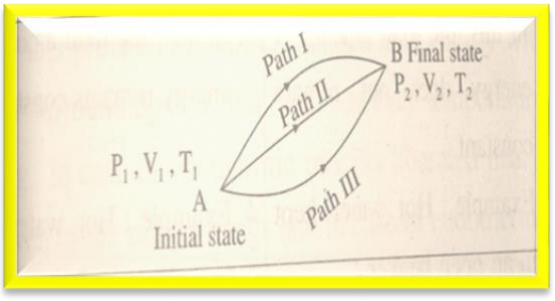
⇨INTENSIVE PROPERTY:- A property which is independent on the amount of matter present in a system is called intensive property.

Examples :- Pressure, temperature, surface tension, viscosity, melting point, boiling point, specific heat.

Q.6 What are STATE VARIABLES:- The measurable thermodynamic properties of a system like pressure , temperature, volume etc are called state variable. When one or more variables change, the system changes to a new state.

Q.7 STATE FUNCTION: - [Define and explain state function]

State function is defined as any property of a system , which depends on current OR only on initial and final state of the system but is independent of the path followed by the system during the thermodynamic process. E.g. Mass, pressure, temperature, volume etc.



Consider a change in a state of a system from initial state A to final state B, changing state functions from P_1, V_1, T_1 to P_2, V_2, T_2 by three different paths. The changes in P, V and T are,

$$\Delta P = P_2 - P_1$$

$$\Delta V = V_2 - V_1$$

$$\Delta T = T_2 - T_1$$

These changes are independent of all three paths but depend only on initial and final states.

Q.8 Define Process and its types : A transition from one equilibrium state to another is called a process.

They are of different types.

i. Isothermal process: It is the process in which temperature of the system remains constant throughout the transformation.

In such process heat flows from the system to surroundings and vice versa so as to keep the temperature constant. For a given temperature the internal energy *(U)* of the system remains constant. Thus, $\Delta T = 0$ and $\Delta U = 0$.

ii. Isobaric process: In isobaric process the pressure remains constant during the transformation. In the laboratory chemical reactions are carried out in open containers at constant atmospheric pressure or $P = 0$

iii. Isochoric process: It is a process during which volume of the system remains constant during the transformation. A chemical reaction carried out in a closed containeris isochoric.In isochoric process since $\Delta V = 0$, no mechanical work is performed. E.g. cooking carried out in a pressure cooker.

iv. Adiabatic process: A process in which there is no exchange of heat between system and surroundings is an adiabatic process. ($Q = 0$). In adiabatic process the system is completely insulated from the surroundings. For an exothermic process the heat is released which rises temperature of the system. If the process is endothermic the temperature falls. This results in either increase or decrease of internal energy.

v. Reversible process:Consider a gas enclosed in a cylinder fitted with a movable piston. Let the external pressure be P_{ext} on the outer surface of the piston be set equal to pressure *P of* the gas. Neither expansion nor compression of the gas occurs. A system is then said to be in mechanical equilibrium with the surrounding.

A process conducted in such a way so that at every stage the driving force is greater than the opposing force due to external pressure (P_{ext}) and which can be reversed by a slight change of the opposing force is reversible process.

Features of reversible process

i. The driving and opposing forces differ by an infinitesimal amount.
ii. The process can be reversed by an infinitesimal change in conditions.
iii. A reversible process proceeds infinitely slowly and takes place in infinite number of steps.
iv. At the end of every step of the process, the system attains mechanical equilibrium with the surroundings.
v. In this process maximum work is obtained.
vi. This is a hypothetical process.

Q.9 Distinguish between isothermal process and adiabatic process.

Isothermal process	Adiabatic process
1. The temperature of the system remains constant. $\Delta T = 0$	1. The temperature of the system changes. $\Delta T \neq 0$
2. The system exchanges heat with the surrounding. $Q = 0$	2. The system does not exchanges heat with the surrounding. $Q \neq 0$
3. Total internal energy of the system remains constant. $\Delta U = 0$	3. Total internal energy of the system remains constant. $\Delta U \neq 0$
4. The system is not thermally isolated.	4. The system is thermally isolated.
5. In this process $Q = -W$	5. In this process $W = \Delta U$
6. $\Delta H = 0$	6. $\Delta H \neq 0$

Q.10 Distinguish between reversible process and irreversible process

Reversible process	Irreversible process
1. The process whose direction can be reversed at any stage by an infinitesimal increase in the opposing force is called a reversible process	1. The process whose direction cannot be reversed by an infinitesimal increase in the process is called an Irreversible process
2. Search a process is not spontaneous and takes place infinitesimally slowly and takes finite time for completion	2. Search a process is spontaneous and takes finite time for completion
3. The thermo dynamic equilibrium is always maintained between the system and the surrounding at every step	3. The Thermodynamic Equilibrium is attained only at the end of the process
4. The opposing force is infinitesimally less than the driving force	4. The opposing force is significantly less than the driving force
5. It is an ideal or hypothetical process	5. It is a practical or real and spontaneous process
6. Maximum work can be derived from such a process	6. Work derived in such process is always less than the maximum work

Q.11 What are the ways of changing the energy of a system?

Ans:- The energy of a system can be changed by

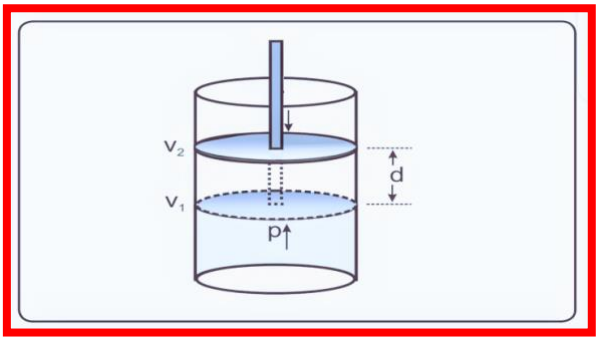
1. **Transfer of energy as work.**
2. **Transfer of energy as heat.**

Q.12 What kind of work is involved in chemical thermodynamics?

Ans:- The type of work involved in chemical thermodynamics is mechanical work or pressure - volume work. This is a work done when the system undergoes a volume change due to expansion or contraction against an external opposing pressure. It is represented as

$W = -P_{ext} (V_2 - V_1)$

Q.13 Derive an expression for pressure - volume work. OR
Derive the expression for work when a gas expands against constant external pressure. OR
Derive the equation $W = -P_{ext} (V_2 - V_1)$



Ans:-

(i) Consider a certain amount of an ideal gas is enclosed in an ideal cylinder fitted with mass less friction less rigid, movable Piston of cross sectional area A at pressure P, occupying volume V1 at temperature T.

(ii) On expansion the force exerted by a gas is equal to area of piston multiplied and opposite in sign to the external atmospheric pressure that opposes the movement and has its value - P_{ext}.

(iii) As the gas expands it pushes the Piston upward through a distance d against external force f pushing the surroundings. The work done by the gas is.....

∴ Work done= - force x displacement (- sign indicates the lowering of energy of the system during expansion)

∴ Work done = - f x d

$= - P_{ex}$ **x area x d →(eq.1)**

but area x displacement = change in volume

$= V2 - V1$

area x d $= \Delta V$ **→(eq.2)**

∴Work done = $- P_{ext} \times \Delta V$ **→(substituting eq.2 in eq.1)**

OR

Work done = $- P_{ext} \times (V_2 - V_1)$

When the gas expands, work is done by the system on the surroundings. Since $V_2 > V_1$, ***W*** **is negative. When the gas is compressed, work is done on the system by surroundings, in this case** $V_1 < V_2$, **and** $-P_{ext} V$ **or** ***W*** **is positive.**

Remember... **during expansion of a gas, work is done by the system on the surroundings and during compression work is done on the system by the surroundings.**

Q.14 Explain the work obtained in vacuum OR Free expansion:

Ans. i) A free expansion means expansion against zero opposing force.

ii) Such expansion occurs in vacuum.

iii) The work done by a system during such expansion is given by Eq.

$W = -P_{ext}(V_2 - V_1)$ When the gas expands in vacuum, there is no opposing force that is P_{ext} and hence, $W = 0$. In other words no work is done when the gas expands freely in vacuum.

Q.15. Explain the concept of heat *(Q)* :

Ans:- i) heat is a form of energy by which the system exchanges energy with its surroundings.

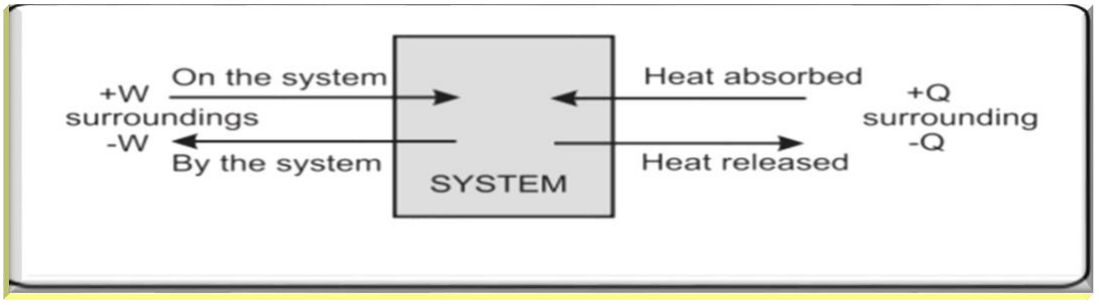
ii) When the system and its surroundings are at different temperatures ; either heat flows in or let out of the system.

iii) heat is not a property of a system hence it is not a state function.

iv) The amount of heat exchanged between system and surroundings depends on the path of process and does not depend on initial and final state of the system . Hence it is a path function.

Q.15. What are the Sign conventions of *W* and *Q:*

Ans:- The energy entering the system from the surroundings has positive value. While the energy leaving the system and flowing into the surroundings is negative. This is shown in Figure below...



***+Q:* Heat is absorbed by the system from the surroundings.**

***-Q:* Heat is released by the system to the surroundings.**

+W: Work is done on the system by the surroundings.

-W: Work is done by the system on the surroundings.

Note *W* and *Q* are path functions

Q.16. Explain the Concept of maximum work. OR

What are the features of isothermal reversible process or maximum work?

i) Eq. $W = -P_{ex} (V_2 – V_1)$ shows the amount of work performed by a system is governed by the opposing force (P_{ext}). Larger the opposing force more work is done by the system to overcome it.

ii) If the opposing force is zero no work is involved. With an increase of the opposing force from zero, more work will be needed by the system. When the opposing force reaches its maximum the system performs maximum work. With an opposing force being greatest more effort would be needed to overcome it.

Features of reversible process

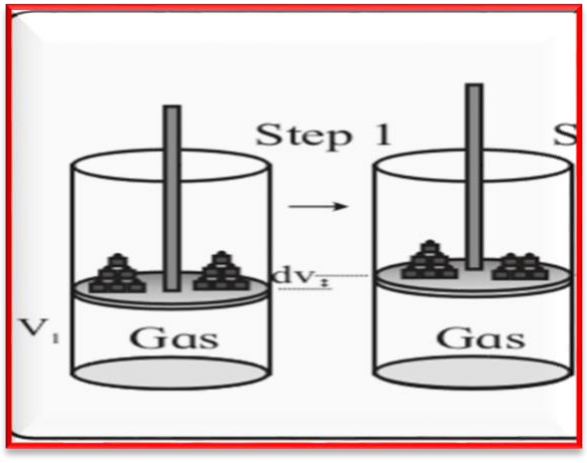
i. The driving and opposing forces differ by an infinitesimal amount.
ii. The process can be reversed by an infinitesimal change in conditions.
iii. A reversible process proceeds infinitely slowly and takes place in infinite number of steps.
iv. At the end of every step of the process, the system attains mechanical equilibrium with the surroundings.
v. This is a hypothetical process.
vi. In this process maximum work is obtained. This is given by

$$W_{max} = -2.303\, nRT \log_{10} \frac{V_2}{V_1}$$

OR

$$W_{max} = -2.303\, nRT \log_{10} \frac{P_1}{P_2}$$

Q.17 Derive the expression for the work obtained in an isothermal reversible expansion of an ideal gas. OR
Derive the expression for maximum work.



Ans:-

(i) Consider n moles of an ideal gas enclosed in an ideal cylinder fitted with a mass less and frictionless movable rigid piston.

(ii) Let V be the volume of the gas and a pressure P and a temperature T.

(iii) For a reversible process and infinitesimally small change is carried out by

decreasing the pressure from P to P - dP so that the volume increases from V to V + dv.

(iv) Then the change in volume will be V +dV – V = dV which is infinitesimal quantity. Hence the work obtained in an infinitesimal step will be,

$dw = -(p - dp)dv$

$= -pdv + dpdv$

$= -pdv$ .....(due to negligible value of dp.dv, the product can be neglected)

$\therefore dw = -pdv$

Integrating the above equation between the limits of initial volume V1 and final volume V2

$\int dw = -\int pdv$

$= -p \int dv$

$\therefore W_{max} = -nRT/V \int_{V1}^{V2} dv$ .....PV=nRT acc. to ideal gas equation

$= -nRT \int_{V1}^{V2} \frac{dv}{V}$

$= -nRT \ln[V]_{V1}^{V_2}$

$= -nRT[\ln V_2 - \ln V_1]$

$= -nRT \ln \frac{V2}{V1}$

$$W_{max} = -2.303nRT\log_{10}\frac{V_2}{V_1}$$

At constant temperature, $P_1V_1 = P_2V_2$

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

$$\therefore W_{max} = -2.303nRT\log_{10}\frac{P_1}{P_2}$$

Interconversion of Units of work and energy.

1 Cal = 4.184 J

1 cal = 0.0413 Latm

1 L atm = 24.22 cal

1 L.atm = 101.3 J

1 atm = 1.013×10^5 Pascals $N\,m^{-2}$ OR

1 Joule = 10^7 erg.

FORMULAS

1] Work done against constant pressure

$$W = -P(V_2 - V_1)$$

2] Work done in Reversible Process

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

OR

$$= -2.303\,nRT \log\left(\frac{P_1}{P_2}\right)$$

3] n = wt. of substance / mol. wt of substance

Q] One mole of a gas expands by 3 L against a constant pressure of 3 atm. Calculate the work done in (a) L.atm (b) Joules (c) Calories → 3 Marks

Given :- $n = 1$ mol
$\Delta V = 3$ L
$P_{ext} = 3$ atm

Find :- Work = ?

Solution :-

(a) $W = -P_{ext} \times \Delta V$
$= -(3 \text{ atm}) \times (3 \text{ L})$
$= -9.0 \text{ L.atm.}$

(b) $\because 1 \text{ L.atm} = 101.3 \text{ J}$
$\therefore W = -9.0 \times 101.3 \text{ J}$
$= -911.7 \text{ J}$

(c) $\because 4.184 \text{ J} = 1 \text{ cal}$
$\therefore W = \frac{-911.7}{4.184}$
$= -217.9 \text{ cal.}$

Ans :- (a) $W = -9.0$ L atm
(b) $W = -911.7$ J
(c) $W = -217.9$ cal.

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2] Three litres of an ideal gas at a pressure of 5 atmosphere expand freely at constant pressure until the volume is 8 litres. How much is the work done in expansion?

Given :- $V_1 = 3L$
$V_2 = 8L$
$P_{ext} = 5$ atm $W = ?$

Solution :-

$W = -P_{ext}(V_2 - V_1)$
$= -5\ (8-3)$
$= -25$ L.atm
$= -25 \times 101.32$ J
$= -2533$ J

Work done = $W = -2533$ J

3] Calculate the work obtained in a process when 1 mole of an ideal gas is compressed isothermally and reversibly from 2.02×10^5 Pa to 20.2×10^5 Pa at 300K. ($R = 8.314\ JK^{-1}mol^{-1}$)

Given :- $n = 1$ mol
$R = 8.314\ JK^{-1}mol^{-1}$
$T = 300$ K
$P_1 = 2.02 \times 10^5$ Pa
$P_2 = 20.2 \times 10^5$ Pa

Solution :- For isothermal reversible compression, work done is given as:-

$W_{max} = -2.303\ n\ R\ T \log_{10} \frac{P_1}{P_2}$

$= -2.303 * 1 \times 8.314 \times 300 \times \log_{10} \frac{2.02 \times 10^5}{20.2 \times 10^5}$

$\log 1 - \log 10$
$= 0.0000 - 1.0000$
$= -1.0000$

$= -2.303 \times 1 \times 8.314 \times 300 \times \log \frac{1}{10}$

$= -2.303 \times 1 \times 8.314 \times 300 \times (-1)$

$\log 2.303 = 0.3623$
$\log 8.314 = 0.9198$
$\log 300 = 2.4771$
3.7592

Antilog $(3.7592) = 5744.0$

$\therefore$ $W_{max} = +5744.0$ J

4] Carbon monoxide expands isothermally and reversibly at 300 K doing 4.754 KJ of work. If the initial volume changes from 10 dm^3 to 20 dm^3, calculate the number of moles of carbon monoxide ($R = 8.314$ J K^{-1} mol^{-1})

Given:- $W_{max} = -4.754$ KJ $= -4754$ J
$n = ?$
$R = 8.314$ J K^{-1} mol^{-1}
$T = 300$ K
$V_1 = 10$ dm^3
$V_2 = 20$ dm^3

Solution:-

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

$-4754 = -2.303 \times n \times 8.314 \times 300 \log \frac{20}{10}$

$-4754 = -2.303 \times n \times 8.314 \times 300 \times \log 2$

$-4754 = -2.303 \times n \times 8.314 \times 300 \times 0.3010$

$\log 1 - \log 10$
$= 0.0000 - 1.0000$
$= -1.0000$

$= -2.303 \times 1 \times 8.314 \times 300 \times \log \frac{1}{10}$

$= -2.303 \times 1 \times 8.314 \times 300 \times (-1)$

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Given:- $W_{max} = -4.754$ KJ $= -4754$ J
$n = ?$
$R = 8.314$ J K^{-1} mol^{-1}
$T = 300$ K
$V_1 = 10\ dm^3$
$V_2 = 20\ dm^3$

Solution:-

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

$-4754 = -2.303 \times n \times 8.314 \times 300 \log \frac{20}{10}$

$-4754 = -2.303 \times n \times 8.314 \times 300 \times \log 2$

$-4754 = -2.303 \times n \times 8.314 \times 300 \times 0.3010$

$$\therefore n = \frac{-4754}{-2.303 \times 8.314 \times 300 \times 0.3010}$$

log 2.303	=	0.3623
log 8.314	=	0.9198
log 300	=	2.4771
log 0.3010	=	$\bar{1}$.4786
		3.2378

log 4754 = 3.6771

AL [log(Numerator) − log(Denominator)]

$\therefore$ 3.6771

− 3.2378

AL [0.4393] = 2.750

∴ Number of moles (n) = 2.750

Q.18 Define and explain the term internal energy

Ans:- Internal energy :- it is defined as the total energy constituting potential energy and kinetic energy of the molecules present in the system.

Explanation:-

(i) The internal energy of a system is a state function and thermodynamics function it is denoted by U

(ii) Its value depends on the state of a system.

(iii) The change in internal energy depends only on initial state and the final state of the system.

(iv) It is an extensive property of the system.

(v) It has same unit as heat and work.

(vi) Total internal energy U of the system is,

Total energy = potential energy + kinetic energy

$U_{Total} = U = U_{potential} + U_{kinetic}$

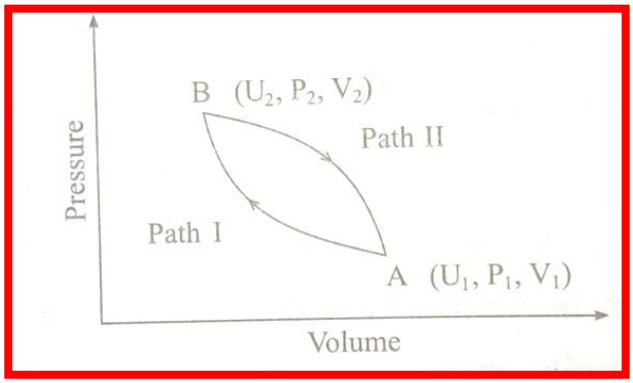
Q.19 Prove that the change in internal energy in a process is independent of path taken
OR ' internal energy is a state function ' explain.

⇨ **Internal energy is defined as Total energy constituting potential energy and kinetic energy of the molecules in the system**

⇨ **State function the properties whose value depends only on initial and final state of the system and are used to define a state of the system completely are called as state functions**

⇨ **Explanation**

(i) consider a system at State A having internal energy U_1 and pressure and volume P_1 and V_1 respectively



(ii) the system is now taken to state B by changing its pressure and volume to P_2 and V_2 respectively by path I. Let the internal energy of the system at B be U_2

(iii) Let the internal change by ΔU_1

(iv) The system is now brought back to state a A by path II by changing its pressure and volume. Let the internal energy change be ΔU_2 .

(v) if the magnitude of ΔU_1 is not the same as the magnitude of ΔU_2 there will be creation or destruction of energy in the process equivalent to

$\Delta U = \Delta U_1 - \Delta U_2$.

it is contrary to the first law of thermodynamics .

(vi) Therefore $\Delta U_1 + \Delta U_2 = 0$ OR $\Delta U_1 = -\Delta U_2$,

Hence the change in internal energy in a process is independent of the path taken and depends only on the initial and final state of the system hence internal energy is a state function.

Q.20 State the first law of thermodynamics in different ways.

Ans:- First law of thermodynamics is given as-

(i) Energy can neither be created nor be destroyed; however it may be converted from one form into another.
(ii) Whenever a quantity of one kind of energy is consumed or disappears an equivalent amount of another kind of energy appears.
(iii) The total mass and energy of an isolated system remains constant although there may be inter conservation of energy from one form to another.
(iv) The total energy of the universe remains constant.
(v) It is impossible to construct a perfect perpetual motion machine i.e a machine which produces work without the use of energy.

Q.21 Give a corollary of first law of thermodynamics.

Ans:- A corollary of the first law of thermodynamics:
The total amount of work or mechanical energy absorbed by a system is quantitatively converted into heat energy and vice versa. OR
There is equivalent between work or mechanical energy and heat energy.

Q.22 Deduce mathematical equation for the first law of thermodynamics. Justify its expression.

Ans:- The first law of thermodynamics is based on the principle of conservation of energy

(i) Consider an ideal gas filled in an ideal cylinder fitted with a frictionless and weightless movable rigid Piston. Let the system at initial state have internal energy U_1 and volume V_1.
(ii) Let the system absorb heat Q from its surrounding so that the energy of the system increases to U_2 and volume to V_2.
(iii) Due to volume change the system performs the work W. Hence Total energy U_2 of the system in the final state is,

$$U_2 = U_1 + Q + W$$

$$U_2 - U_1 = Q + W$$

(iv) Now internal energy change ΔU is

$$\Delta U = U_2 - U_1$$

$$\therefore \Delta U = Q + W$$

This is the mathematical expression for first law of thermodynamics from the point of view of conservation of energy this expression justifies first law of thermodynamics.

(v) For infinitesimally small change the mathematical expression is,

$$dU = dq + dW$$