Chapter = 6

Thermodynamics

⇒ Thermodynamics :

The study of the flow of mass, heat and energy is the study of thermodynamics.

⇒ Thermodynamics terminology :

- **System :**

A notable part of the universe that is kept under observation is known as the System.

- **Surrounding :**

The remaining part of the universe except for the system which isn't kept under observation is known as surroundings.

In general, it can be stated as;

Universe = System + Surrounding.

- Types of the system

@ Open system :

The system where the flow of the mass and heat energy takes place.

Example : Human body.

(b. Closed system :

The system where the flow of heat energy takes place but has constant mass.

Example : Pressure cooker.

C. Isolated system :

The system where none of the flow takes place.

Example : Thermos flask.

State of the system :

The state of the system can be defined and changed with respect to the changes in state variables i,e, P, V, T and n. These variables define the conditions of the system and change in any one of them, with change the state of the system.

Properties of the system :

- Intensive properties :

Properties depending upon concentration and are independent of mass or the total number of particles in the system. They are pressure refractive index, density etc.

- Extensive properties :

Properties depending upon the mass or the total number of particles in the system. They are volume, total energy, etc.

State and path function:

- State function –

The function will be independent of the path followed but will depend upon the initial and final states while bringing up the changes in the system.

Example: internal energy, enthalpy etc.

- Path function:

The function will depend upon the path followed white bringing up the change in the system.
Example: work, heat, ete .

⇛ Theormodynomic equilibrium :-

The system remain in equilibrium when the state variables do not change and the below three of equilibrium are satisfied.

⇛ Mechanical Equilibriu :-

The absence of mechanical motion, constant pressure and volume bring up the mechanical equilibrium.

⇛ Thermal Equilibrium :-

The constant heat and temperature with a respect to time bring up thermal equilibrium.

⇛ Chemical equilibrium :-

The rate of forward reaction equal to the rate of backward bring up the chemical equilibrium.

⇛ Internal energy :-

The Sum total of the components of the energy influenced by the internal factors of the system is Known as internal energy ; often denoted by U or E.

The system under observation acts as an ideal gas system that depends only upon Kinetic energy and hence, is the function of temperation as $U \propto T$. Thus, the internal energy is a state function.

→ Modes of energy transport :-

→ Heat -

The energy transferred due to temprature different within the system and Surrounding is Known as heat (Q). When the system is heated, the Kinetic energy of the molecules is being energy of the molecules ~~is~~ being increases Which then increases the internal energy.

→ Work -

The energy spent to overcome the external forces acting upon the system is known as work (w). When a system expands, the internal energy is reduced. Whereas, on the contraction of the system the internal energy is increased.

➔ The first law of thermodynamics :-

The first law of thermodynamics states That energy can neither be created nor destroyed.

$$\Delta U = Q + W$$

The Sign conventions are given as ;

Work done by the system = $-W$
Work done on the system = $+W$
Heat flows into the system = $+Q$
Heat flows out of the system = $-Q$

➔ Reversibility :-

The process can Change its direction by very small i.e., infinitesimal change in the system or surrounding ; retracking its original path reaching the same initial state. In a process to follow reversibility, there must not be any dissipative force and the system must be in Quasi-static state.

Quasi - static state -

Here, the system seems to be static at time intervals but not actually in reality. The motion is so slow that the system seems to be in equilibrium with the surroundings.

Expansion Work :-

The work done due to changes in the volume of the system is known as expansion or compression, we take external pressure as the driving force.

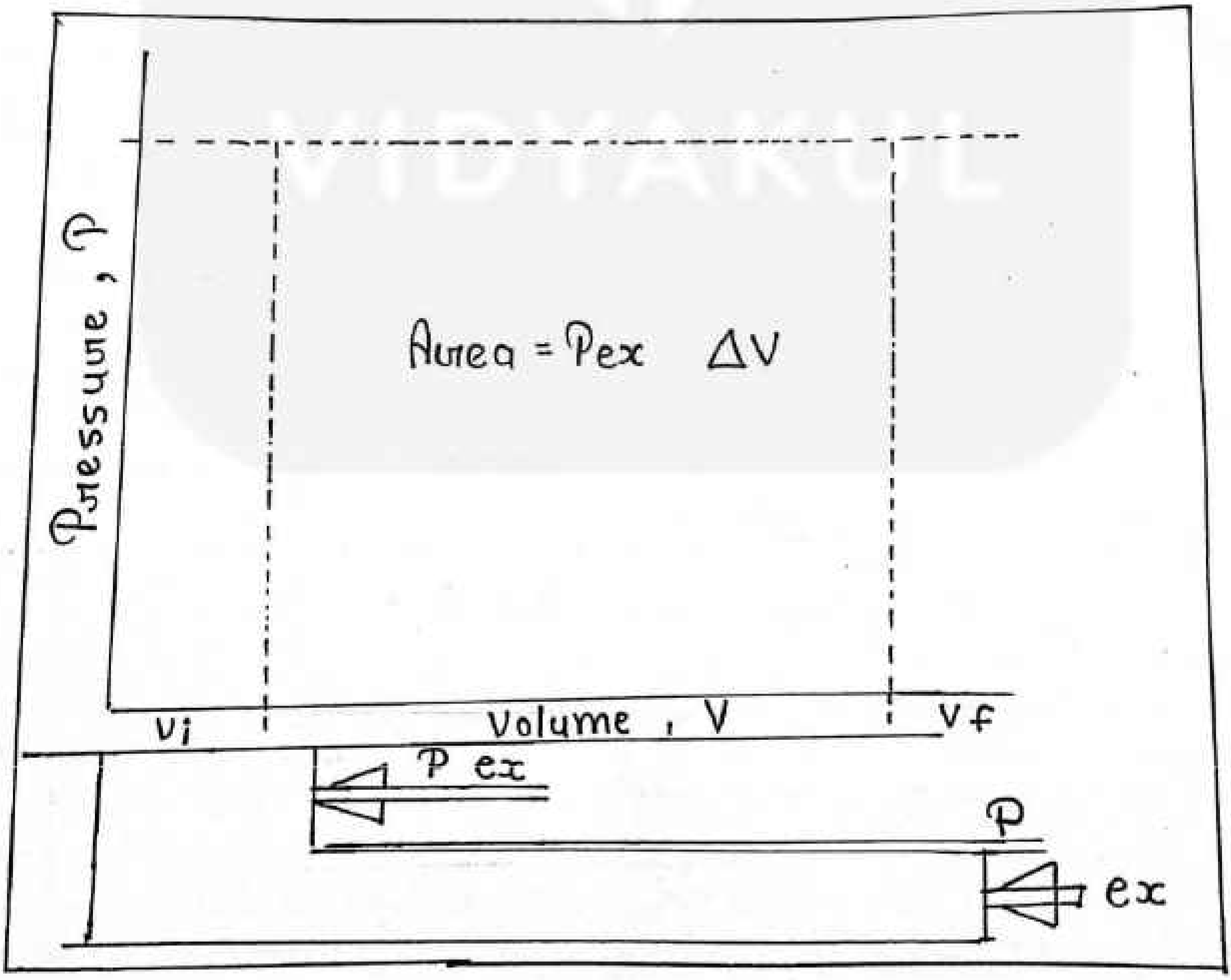
Mathematically, it can be represented as

$$W = \int P_{ex}\, dV$$

four reversible process, external pressure is considered equal to the pressure of the gas. Thus,

$$W = -\int P_{gas}\, dV$$

When a P-V graph is drawn, work done is represented as the area covered under is as shown ;



Expansion Work

➔ Sign Conventions :-

- **W -**

Positive if the volume of the system is decreasing and negative when the volume of the system is increasing.

- **ΔU -** When the temperature of the system or product pressure or volume is reducing, it is negative ; else is positive.

- **Q -**

This needs to be determined by the first low of thermodynamics.

➔ Cyclic process :-

A process that comes back to its original and intial state is known as a cyclic process. A closed graph determines that process and here, $\Delta U = 0$ and $Q_{net} = -W_{net}$.

✦ Enthalpy :-

A thermodynamic state function is defined as the sum of energy stored in the system and the energy used in doing work. Mathmatically, can be represented as ;

$$\Delta H = U + PV$$

- At constant P, $\Delta H = Q_p$.
- At constante V, $\Delta U = Q_v$.

⇒ Molar heat capacity :-

• At constant Pressure :-

The amount of heat needed to raise the temperature of one mole of gas by a degree at constant pressure. It can be stated as ;

$$C_p = \frac{Q_p}{n \Delta T}$$

• At constant volume :

At The amount of heat needed to raise the temperature of one mole of gas by a degree at constant volume . It can be Stated as :;

$$C_V = \frac{Q_v}{n \Delta T}$$

we can now say that, $\Delta H = n C_p \Delta T$ and $\Delta U = n C_v \Delta T$.

⇒ Types of thermodynamic process :-

- **Isothermal process :**

The constant temperature process is known as the isothermal process. Here , $\Delta U = 0$ and $\Delta H = 0$

$$W = -2.303 n RT \log \frac{V_2}{V_1} = -2.303 n RT \log \frac{P_1}{P_2}$$

$$Q = 2.303 n RT \log \frac{V_2}{V_1} = 2.303 n RT \log \frac{P_1}{P_2}$$

- **Adiabatic process -**

When the heat exchanged with the surrounding is zero, such a process is known as adiabatic process. Here,

$T V^{\gamma-1} = C, T^{\gamma} P^{1-\gamma} = C, P V^{\gamma} = C$

Where, C is constant.

$$Q = 0 \Rightarrow W = \Delta U$$

Now,

$$\Delta U = n C_v \Delta T = \frac{(P_2V_2 - P_1V_1)}{(\gamma - 1)}$$

$$= \frac{(nR\Delta T)}{(\gamma - 1)}$$

and

$$\Delta H = n C_p \Delta T$$

- Isochoric Process :

Constant volume process is known as isochoric process. Here, $W = 0$,

$\Delta H = n C_p \Delta T$

$\Delta U = n C_v \Delta T = Q_v$.

- Isobaric process :-

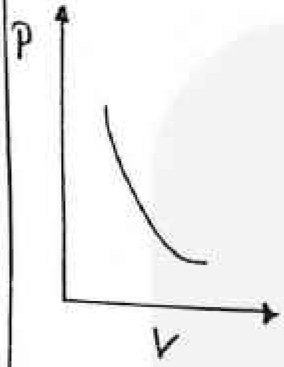
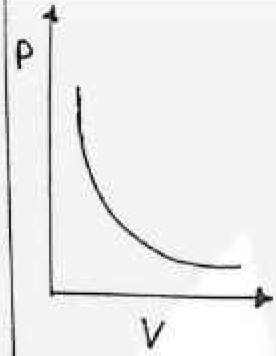
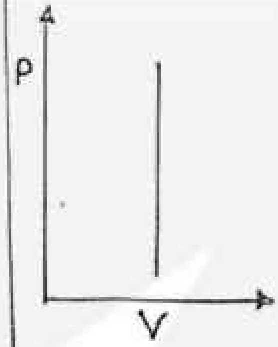
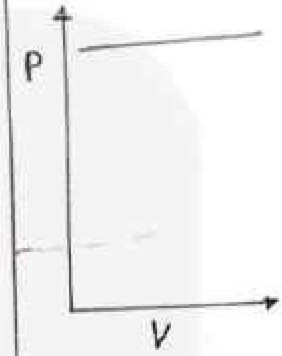
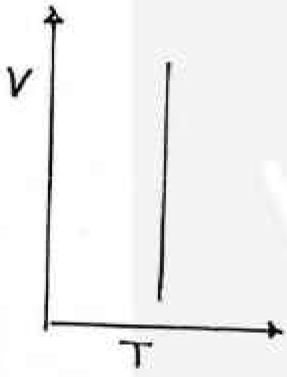
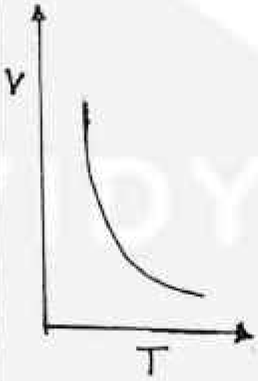
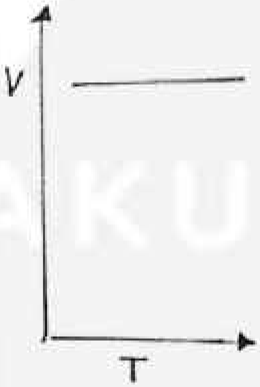
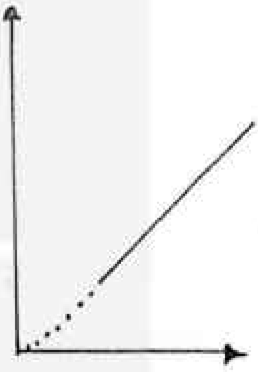
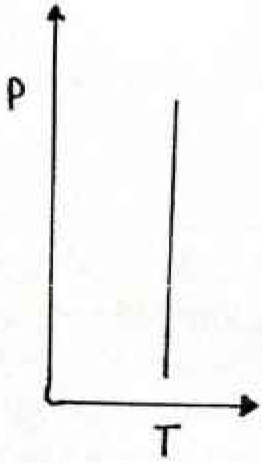
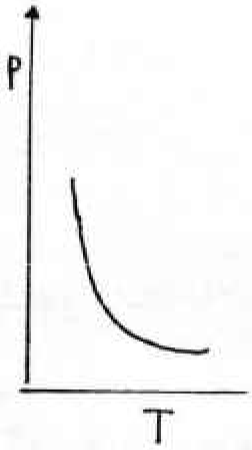
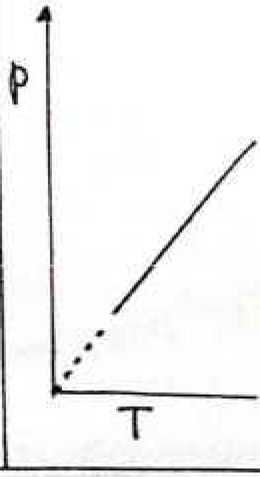
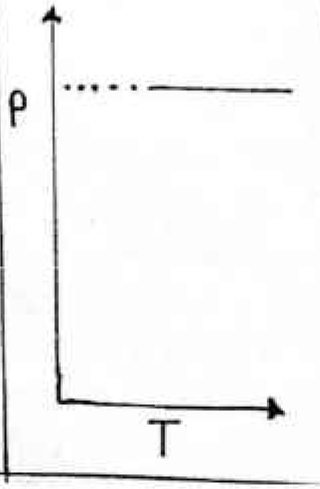
Constant pressure process is known as isbaric process here,

$W = -P\Delta V = -nR\Delta T$,

$\Delta H = n C_p \Delta T = Q_p$ and

$\Delta U = nC_v\Delta T.$

Graphs :-

Isothermal	Adiabatic	Isochoric	Isobaric
			
			
			

Graph to Thermodynamic processes

Note that, the P-V graphs of the isothermal and adiabatic processes are similar but one for adiabatic is steeper that the of isothermal.

- Irrevesible process :

Work done is given as $W = -\int P_{ex} dv$ in the irreversible process. Here, we cannot say external pressure will be equal to that of the pressure of the gas.

- Free expansion :

In free expansion, the external pressure of the gas is zero i.e., the gas expandin against the vacuum will have work be supplie to the process showing no changes in the temperature. Hence, it is an isothermal and adiabatic process.

- Polytropic process :

A generalised form of any thermodynamic process can be represented as PV^n = constant.
for the isothermal process, $n = 1$,
for adiabatic process, $n = \gamma$.

→ Thermochemical equation :-

A chemical equation giving you all the informati like phases of reactants and products in the reaction along with the same is know as a thermochemical equation.

→ Types of Reaction :-

• Endothermic reaction -

The Chemical reaction that absorb energy are known as endothermic reaction.
Here, $\Delta H = +$ ve.

• Exothermic reaction -

The Chemical reaction that release energ are known as exothermic reactions.
Here, $\Delta H = -$ve.

four any Chemical reaction,

ΔH Reaction = ΔH products - ΔH reaction

This Change in enthalpy occurs due to making and breaking of bonds.

⇛ Hess law of Constant heat Summation:-

four a reaction that takes place in a Stepwise manner, the net Change in enthalpy Changes can be calculated as the enthalpy Changes in each step. The governing law is known as the Hess law of Constant heat summation.

➧ Enthalpy of reactions:-

• Enthalpy of bond dissociation:

The energy needed to break the bonds of one - mole molecules is know as the enthalpy of bond dissociation. It is defined per mole of the molecule.

• Enthalpy of combustion:-

the heat released or absorbed when a mole of a Substance undergoes combustion in presence of oxygen in Known as Enthalpy of Combustion.

- **Enthalpy of formation:**

the heat released or absorbed when a mole of an compound is formed from its constituent elements under their Standard elemental forms is Known as enthalpy of formation.

- **Enthalpy of atomization:**

The energy required to convert any Substance to gaseous atoms is Known as the enthalpy of atomization. It is defined per mole of the gaseous atoms.

- **Enthalpy of Sublimation:**

The heat required to Change a mole of a Substance from Solid - state to its gaseous state at STP is Known as enthalpy of Sublimation.

- **Enthalpy of phase transition:**

The phase transition from one phase to another release or absorbs a particular Standard enthalpy which is known as enthalpy of phase transition.

- **Enthalpy of ionization:**

The amount of energy an isolated gaseous atom will take to lose an electron in its ground state is known as the enthalpy of ionization.

- **Enthalpy of the Solution:**

The heat released or absorbed when a mole of a compound is dissolved in excess of a Solvent (mostly, water) is known as enthalpy of Solution.

→ **Enthalpy of dilution:**

The enthalpy change associated with the dilution process of a component process of a component in a Solution at constant pressure is known as enthalpy of dilution. It is defined as energy per unit mass or amount of substance.

⇛ The Second law of thermodynamics :-

The state of entropy of the entire universe, as an isolated system will always increase over time, is the standard statement of the second law of thermodynamics.

• Need :

the first law of thermodynamics: state the conversion of energy in a process but does not explain the feasibility of the need for the second law of thermodynam

⇛ Types of processes :-

- **Spontaneous process:**

The spontaneous process has the tendency to take place naturally and no external work is needed to carry out the same.

- **Non-Spontaneous process:**

The non-spontaneous process is driven by external work and cannot be performed naturally.

Entropy :-

The measure of randomness or disorder in the process of a body is known as its entropy. It is a state function and is represented as S.

The spontaneous process is the process in which the total randomness of the universe tends to increase. Thus,

$$\Delta S = \frac{Q_{rev}}{T}$$

for Spontaneous change,

$$\Delta S_{Total} = \Delta S_{system}.$$

$+ \Delta S_{surrounding} > 0$

for reversible processes where the entropy of the universe remains constants,

$\Delta S_{Total} = 0.$

⇒ Entropy Change in thermodynamics process:-

The entropy change in any thermodynamics process can be mathematically represented as;

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

- **Isothermal process:**

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

- **Isochoric process:**

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

- **Isobaric process:-**

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

- **Adiabati Process:**

$$\Delta S = 0$$

→ Gibbs free energy

This gives us the most convenient parameter to judge the perspective of the system.

At constant temperature it can be represented as:

$$\Delta G_{sys} = \Delta H - T\Delta S_{sys}$$

At constant temperature and pressure

$$\Delta G = -T\Delta S_{Total}.$$

for the process to be spontaneous,

$\Delta G < 0$.

→ Third law of Thermodynamics:

The entropy of the system will approach a constant value as its temperature approaches absoulte zero is the empirical statement of the third law of Thermodynamics.

→ Born Haber Cycle

Born Haber cycle is the process of creation of ionic compounds from the elements in a series of steps. It is a indicative of the factors that are favourable for the formation of ionic bonding.