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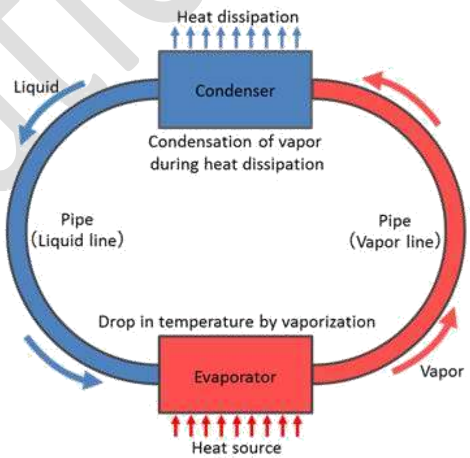
THERMODYNAMIC

Chapter: - 12th



PHYSICS
CLASS: - 11TH
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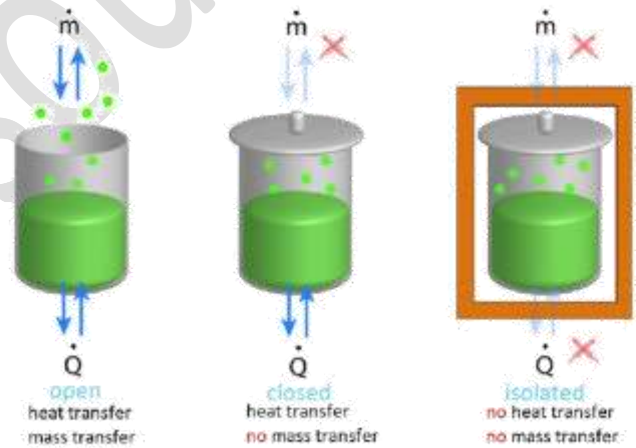
<u>Chapter: - 12th</u>
<u>Thermodynamic</u>

I. **<u>Thermodynamics: -</u>** Thermodynamics is a branch of physics that deals with the relationships between heat, energy, and work. In thermodynamics, the term "system" refers to a defined portion of the universe that is under study, while everything outside that system is considered the surroundings.

Based on boundaries and content, thermodynamic systems can be classified as:

1. **<u>Open System:</u>** This type of system can exchange both energy (like heat and work) and matter with its surroundings.
   <u>An example</u> would be boiling water in an open pot. The water can absorb heat from the stove (energy transfer), and steam can leave the pot (mass transfer).

2. **<u>Closed System:</u>** This type of system can exchange energy (heat and work) but not matter with its surroundings.
   <u>An example</u> would be water boiling in a sealed pot. The water can absorb heat from the stove, but no mass (like steam) can escape or enter the pot.



thermodynamic systems

3. **<u>Isolated System:</u>** This type of system cannot exchange either energy or matter with its surroundings.
   <u>An example</u> in theory would be a thermos flask that's perfectly sealed and perfectly insulating (though in practice, no system is perfectly isolated).

4. **<u>Adiabatic System:</u>** This system does not exchange heat with its surroundings but can exchange work. Energy can still be transferred through work. A rapid compression or expansion of a gas where no heat exchange can occur in the short time frame can be approximated as an adiabatic process.

The boundary that separates the system from its surroundings can be real or imaginary and can be rigid or flexible, depending on the requirements of the study or experiment.

II. Thermodynamic Equilibrium: -

In thermodynamics, equilibrium refers to the state in which all the properties of a system are unchanging over time. When a system is in thermodynamic equilibrium, there's no net flow of matter or energy within the system. It is important to note that equilibrium does not imply inactivity, but rather a balance in which activities or processes are ongoing, but they cancel each other out.

There are several types of thermodynamic equilibrium:

1. **Mechanical Equilibrium:** This is achieved when there's no unbalanced forces within the system or between the system and its surroundings. For example, two connected chambers containing gas will be in mechanical equilibrium when the pressure in both chambers becomes equal.

2. **Thermal Equilibrium:** When two systems are in thermal equilibrium, there's no net flow of heat between them. This means they are at the same temperature. If you place a hot object in contact with a cold one, they will eventually reach thermal equilibrium, resulting in both objects having the same temperature.

3. **Chemical Equilibrium:** This refers to the state where the concentration of reactants and products does not change over time. At this point, the rate of the forward reaction equals the rate of the reverse reaction.

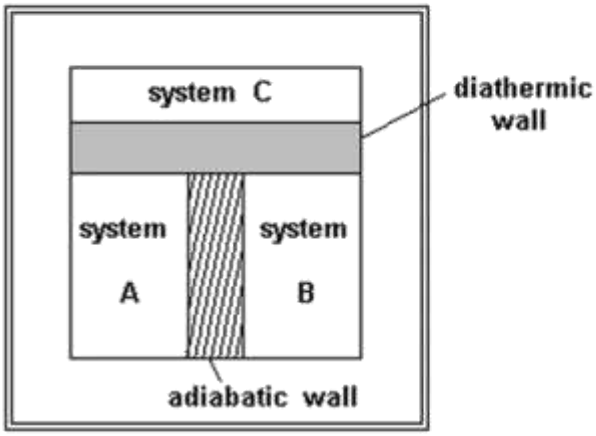
4. **Phase Equilibrium:** When the amount of substance in each phase (like solid, liquid, and gas) remains constant over time, the system is said to be in phase equilibrium. An example is when the rate of evaporation of a liquid equals the rate of its condensation.

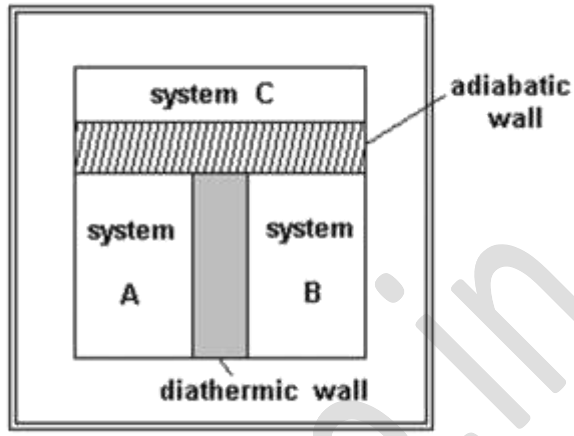
5. **Radiative Equilibrium:** This type of equilibrium refers to a balance between the absorption and emission of radiation.

   When a system is in simultaneous mechanical, thermal, chemical, and phase equilibrium, it's said to be in complete thermodynamic equilibrium.

III. Zero Law of Thermodynamics: -

The zeroth law of thermodynamics states that if two systems A and B are separately in thermal equilibrium with a third system C, then A and B are in thermal equilibrium with each other.





IV. Internal energy, Heat, and Work: -

- ✓ **Internal energy:** - Internal energy of a system is defined as the total energy possessed by the system due to molecular motion and molecular configuration. It is represented by U.

1. **Internal Kinetic Energy (U_k):**
   - **Translational motion**: This refers to the straight forward movement of molecules in a straight line.
   - **Rotational motion**: This pertains to the rotation of molecules around an axis.
   - **Vibrational motion**: This involves the periodic motion of atoms within a molecule, where they move towards and away from each other.

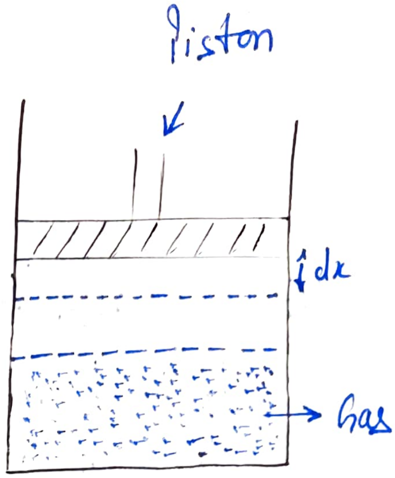
2. **Internal Potential Energy (U_p):**
   - This energy arises due to forces between the molecules or atoms. These can be attractive or repulsive forces and vary depending on the distance between the molecules or atoms.
   - In gases, for instance, potential energy is often associated with interactions between molecules when they come close to one another during collisions.
   - In solids, the potential energy can be due to the position of the atoms within a crystal lattice.

$$U = U_k + U_p$$

Thus, the sum of molecular kinetic and potential energies in the frame of reference relative to which the center of mass of the system is at rest. Internal energy of a real gas is the sum of internal kinetic energy and internal potential energy of the molecules of the gas.

Work :-

Suppose a gas is Confined in a cylinder with a movable Piston, if (P) Pressure on the piston and (A) is area of Piston, the force by the gas on the Piston of cylinder



$$F = PA \quad \text{—(I)}$$

when the Piston is pushed outward a distance dx, then the work done by the gas

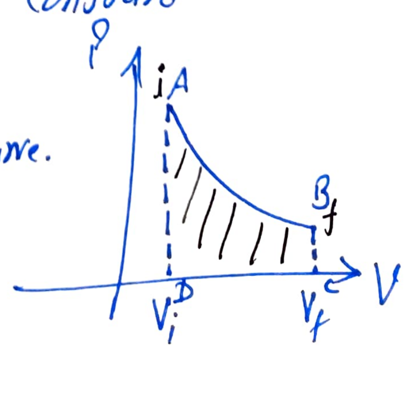
$$dw = F dx$$
$$dw = P A dx$$
$$dw = P dV \quad \text{—(II)} \quad [\because A dx = dV]$$

for a finite volume from V_i to V_f

$$\text{work done is } dw = \int_{V_i}^{V_f} P (dV)$$

Here P may be variable or constant

$$\text{work done} = \int_D^C \text{Area of strip or curve.}$$



$$\boxed{W = \text{Area } ABCDA}$$

Ways to Change Internal Energy of a System There are four ways to change the internal energy of a system.

- **(i)** By doing work on the system (ΔW = -ve).
- **(ii)** If system is doing some work (ΔW = +ve).
- **(iii)** If some heat energy is given to the system (ΔQ = +ve).
- **(iv)** If some heat energy is taken out from the system. (ΔQ=-ve).

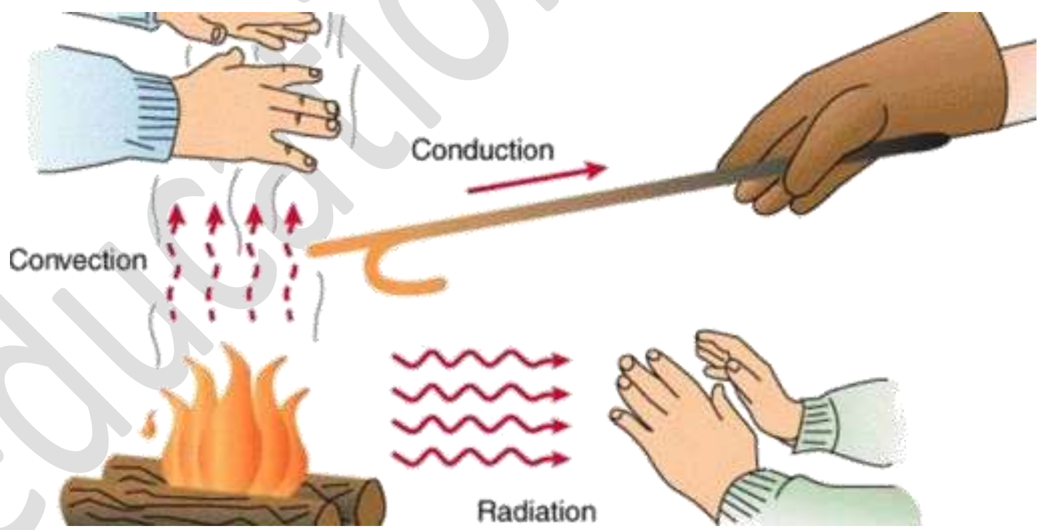
✓ **Heat: -** It is the energy that is transferred between a system and its environment because of the temperature difference between them.

SI unit of heat is **joule(J)**.

The amount of heat Q given to a body to raise its temperature from T_i to T_f depends on mass, nature of substance and change in its temperature.

$$\Delta Q \propto m(\Delta T)$$
$$\Delta Q \propto m (T_f - T_i)$$
$$\Delta Q = m\, s\, (T_f - T_i)$$

where, m = mass of body,
T_i = initial temperature, T_f = final temperature,
s = specific heat of material.



V. First Law of Thermodynamics: -

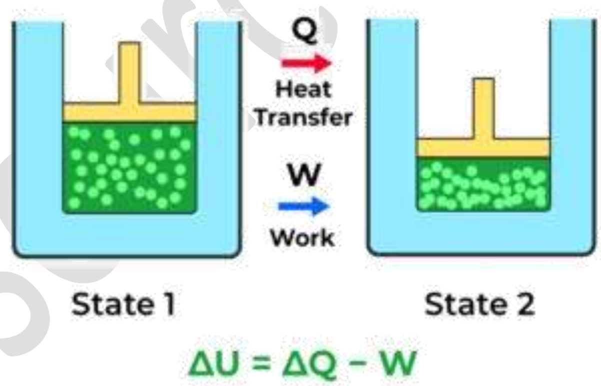
The First Law of Thermodynamics, also known as the Law of Energy Conservation, states that energy cannot be created or destroyed in an isolated system. The total amount of energy in a system is constant, although it can change from one form to another (e.g., from potential to kinetic energy or vice versa).

Also, according to first law of thermodynamics, whenever heat is added to a system, it transforms to an equal amount of energy in some other form.

$$\Delta U = \Delta Q - \Delta W$$

Where:

- ΔU is the change in internal energy of the system.
- ΔQ is the heat added to the system **(positive when heat is added to the system and negative when heat is removed from the system).**
- ΔW is the work done by the system **(positive when work is done by the system on its surroundings and negative when work is done on the system by its surroundings).**



Thus, according to first law of thermodynamics, the energy (ΔQ) supplied to a system increases partly the internal energy of the system (ΔU) and the rest is spent in doing work on the environment (ΔW).

Limitation of first Law of thermodynamics: -

- ❖ **The first law does not indicate the direction in which the change can occur.**
  When a moving car is stopped by applying brakes, work done against friction is converted into heat. When the car cools down, it does not start moving with the conversion of all its heat energy into mechanical work.

- ❖ The first law gives no idea about the extent of change.
- ❖ The first law of thermodynamics gives no information about the source of heat. i.e., whether it is a hot or a cold body.

(a) Change of condition of gaseous state –

i. **Isothermal: -** In an isothermal process, temperature remains constant. If the system is an ideal gas, whose internal energy U depends only on temperature, the internal energy shall remain constant, i.e., **ΔU = 0.**

The first law of thermodynamics implies

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

∴ Heat supplied in an isothermal process is used entirely to do work against the external surroundings.

ii. **Adiabatic Process: -** In an adiabatic process, no heat energy enters or leaves the system as it is well insulated, i.e., **ΔQ=0.**

The first law of thermodynamics implies

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

∴ When a gas expands adiabatically, ΔW is positive. Therefore, ΔU must be negative, i.e., internal energy of the system would decrease and the gas will be cooled. The reverse is also true.

iii. **Cyclic Process: -** In such processes, the system returns to its initial state after any number of changes. In that case, no intrinsic property of the system would change. **ΔU = 0.**

According to the first law of thermodynamics

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

∴ Network done during a cyclic process exactly equals the amount of heat energy transferred.

(IV) Relation between two principal specific Heats of a gas (Mayer's formula) or C_p, C_v Relation :-

Let us consider one gram mole of an ideal gas enclosed in a cylinder.

Let P, V, T be the initial Pressure, volume and Temperature of the gas.

Amount of heat energy supplied at constant volume

$$dQ = C_v\, dT$$

[C_v = molar specific heat]

A constant volume ($dV = 0$)

$$dW = P\,dV = 0$$

According to first law of thermodynamics

$$dQ = dU + dW$$

$$dQ = dU$$

$$dU = C_v\, dT \quad \text{——— (1)}$$

Now heat at constant pressure

$$dQ' = C_p\,dt$$

$[C_p$ = molar specific heat$]$

$$[dW' = P\,dv]\ [$$

According to first law of thermodynamics

$$dQ' = dU' + dW'$$

$$C_p\,dt = dU' + P\,dv \quad \text{——} \quad (II)$$

if dt is same in both cases than dU is also same. i.e $dU' = dU$

Put the value of (I) in (II)

$$C_p\,dt = C_v\,dt + P\,dV$$

$$(C_p - C_v)\,dt = P\,dV \quad \text{——} \quad (III)$$

Acc. to standard gas equation

$$PV = RT$$

$$P\,dv = R\,dT \quad \text{——} \quad (IV)$$

from (III) and (IV)

$$(C_p - C_v)\, dT = R\, dT$$

$$\boxed{C_p - C_v = R}$$

VII Second law of Thermodynamics :-

According to this law, heat flows spontaneously from a substance at high temperature to low temperature.

a) Kelvin Planck statement :- It is impossible to construct a heat engine which would absorb heat from a reservoir and convert 100% into work.

b) Clausius statement :- It is impossible to design a self acting machine unaided by any external agency, which would transfer heat from lower temperature to higher temprature.

<u>Reversible and Irreversible Processes: -</u>

i. **<u>Reversible Process</u>**

A process which could be reserved in such a way that the system and its surrounding returns exactly to their initial states with no other changes in the universe is known as reversible process.

e.g., If heat is absorbed in the direct process, then same amount of heat should be given out in the reverse process. If work is done on the working substance in the direct process, then the same amount of work should be done by the working substance in the reverse process.

The conditions for reversibility are: -

- There must be complete absence of dissipative forces such as friction, viscosity, electric resistance etc.
- The direct and reverse processes must take place infinitely slowly.
- The temperature of the system must not differ appreciably from its surroundings.

ii. **<u>Irreversible Processes</u>**

A process, which does not satisfy even one of the conditions for reversible process is called an irreversible process.

all spontaneous processes of nature are irreversible processes. **For example,** transfer of heat from a hot body to a cold body, ordinary expansion of a gas, diffusion of gases, stopping of a moving body through friction etc. are all irreversible processes.

Irreversibility arises mainly from two causes: -

(a) Many processes like free expansion or an explosive chemical reaction take the system to non-equilibrium states.
(b) Most processes involve friction, viscosity and other dissipative effects.

Some Additional Example: -

i. The decay of organic matter is an irreversible process.
ii. Rusting of iron is an irreversible process.
iii. Most of the chemical reactions are irreversible, because they involve changes in the internal structure of the constituents.