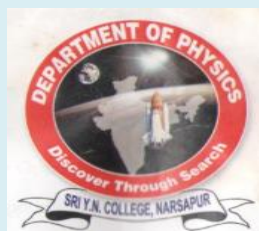




**II BSC SEMESTER-III**  
**HEAT AND THERMODYNAMICS**  
**PHYSICS STUDY MATERIAL**



**2022-2023**

**Department of Physics**  
**Sri Y.N.College (A)**  
**Narsapur**

# UNIT - I

## KINETIC THEORY OF GASES

### LONG ANSWER QUESTIONS

**Q. 1. Derive an expression for Maxwell's law of distribution of molecular speeds in a gas ?**

**Ans :** The law of distribution of velocities was first guessed and partially established by Clark Maxwell, the proof of which by direct methods was given by Boltzmann. The law is known as the *Maxwell-Boltzmann's distribution law for the molecular velocities*. Maxwell and Boltzmann's utilizing probability considerations, have in fact shown that the actual distribution of molecular velocities depends upon the temperature and molecular weight of a gas.

In order to derive the Maxwell-Boltzmann's law.

Let the gas molecules be assumed to obey the following conditions;

1. The velocities along the three perpendicular co-ordinate axes are independent of each other.
2. The probability that any molecule selected at random has velocities lying between certain limits is purely a function of the velocity and of the limits considered.

Consider a gas containing  $n$  molecules per unit volume. Suppose  $n_u$  is the number of molecules having component velocity  $u$  along  $x$ -direction. Then the number of molecules having component velocities lying between  $u$  and  $u + du$  is  $n_u du$ . It can also be shown that the probability of molecule having some component of velocity in a particular direction is a function of that component. The probability of a molecule having  $X$ -component between  $u$  and  $u + du$  is  $f(u) du$ . Similarly the probability of a molecule having  $Y$ -component between  $v$  and  $v + dv$  and  $Z$ -component between  $w$  and  $w + dw$  are respectively  $f(v) dv$  and  $f(w) dw$ .

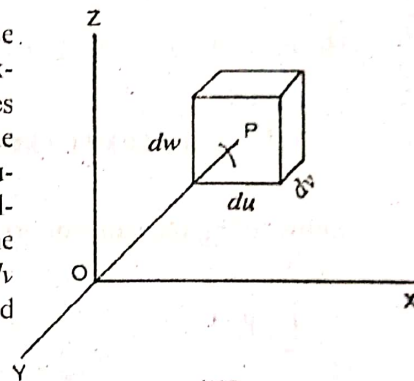


fig.

So the probability of " $n$ " molecules having components of velocity between  $u$  and  $(u + du)$ ,  $v$  and  $(v + dv)$ ,  $w$  and  $(w + dw)$  simultaneously is

$$f(u) f(v) du dv dw.$$

Such probability of  $n$  molecules is  $nf(u) f(v) f(w) du dv dw$ . Now let us represent all the molecules in a velocity diagram with  $OX$ ,  $OY$ ,  $OZ$ , as the coordinate axes along which the component  $u$ ,  $v$ ,  $w$  of the velocity  $C$  are respectively measured. Thus a molecule having the velocity components  $u$ ,  $v$ ,  $w$  will be represented by a point " $P$ " whose coordinates are  $u$ ,  $v$ ,  $w$ . Such a point is called a velocity point. All the molecules whose velocity components lie in the range  $u$  and  $(u + du)$ ,  $v$  and  $(v + dv)$ ,  $w$  and  $(w + dw)$  molecules in  $nf(u) f(v) f(w) du dv dw$ .

These molecules will have the resultant velocity  $C$  where

$$C^2 = u^2 + v^2 + w^2$$

$$nf(u) f(v) f(w) = nF(C) = \phi(C^2) \quad \text{.....(1)}$$

Hence  $F$  and  $\phi$  are some other functions.

Differentiating the equation (1).

$$nf(u) f(v) f(w) du + nf(u) f(v) f(w) dv + nnf(u) f(v) f(w) dw = 0$$

Dividing by  $nf(u) f(v) f(w)$  we get

$$\frac{f'(u)}{f(u)} du + \frac{f'(v)}{f(v)} dv + \frac{f'(w)}{f(w)} dw = 0 \quad \text{.....(2)}$$

Differentiating  $C^2 = u^2 + v^2 + w^2$



$$2u \, du + 2v \, dv + 2w \, dw = 0$$

$$u \, du + v \, dv + w \, dw = 0$$

Multiplying the above expression by a constant  $\lambda$

$$\therefore f(u) = A e^{-\frac{\lambda u^2}{2}}$$

Similarly,  $f(v) = A e^{-\frac{\lambda v^2}{2}}$

$$f(w) = A e^{-\frac{\lambda w^2}{2}}$$

$$\therefore f(u) f(v) f(w) = A^3 e^{-\frac{\lambda(u^2 + v^2 + w^2)}{2}} \quad \dots\dots(5)$$

The constant A and  $\lambda$  can be calculated by integrating the above equation applying the boundary conditions.

Here "n" be the number of molecules per c.c. the molecules move with all velocities ranging from  $-\infty$  to  $+\infty$ . Then the number of molecules per c.c with velocity components between  $u$  and  $(u + du)$ ,

$v$  and  $(v + dv)$ ,  $w$  and  $(w + dw)$  is  $n f(u) f(v) f(w) \, du \, dv \, dw$

$$\text{Hence } n \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(u) f(v) f(w) \, du \, dv \, dw = n$$

$$\therefore \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f(u) f(v) f(w) \, du \, dv \, dw = 1$$

Substituting the value of  $f(u) f(v) f(w)$ , we get

$$\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} A^3 e^{-\frac{\lambda}{2}(u^2 + v^2 + w^2)} \, du \, dv \, dw = 1$$

The value of definite integral  $\int_{-\infty}^{+\infty} e^{-bx^2} \, dx = \sqrt{\frac{\pi}{b}}$

From the above we can write,  $A^3 \left( \frac{\pi}{\lambda/2} \right)^{\frac{3}{2}} = 1$

Putting  $\frac{1}{2} \lambda = B \quad \therefore A^3 \left( \frac{\pi}{B} \right)^{\frac{3}{2}} = 1$

$$\therefore A^3 \left( \frac{B}{\pi} \right)^{\frac{3}{2}} \text{ or } A = \left( \frac{B}{\pi} \right)^{\frac{1}{2}} \quad \dots\dots(6)$$

To determine the value of B, let us consider the pressure exerted by the gas. Let "m" be the mass of each molecule.

As the molecules strike the wall in the YZ plane with the velocity  $u$  and rebound, the rate of change of momentum =  $2mu \, (u n_u \, du)$

$$\text{Total change of momentum} = 2m \int_0^{\infty} u^2 n_u \, du$$

$$\text{But } n_u = n f(u) = n e^{-\frac{\lambda}{2}u^2} = n \sqrt{\frac{B}{\pi}} e^{-\frac{\lambda}{2}u^2}$$

$$\therefore \text{Pressure} = 2mn \sqrt{\frac{B}{\pi}} \int_0^{\infty} e^{-\frac{\lambda}{2} u^2} du$$

$$\therefore \text{Pressure} = P = 2mn \sqrt{\frac{B}{\pi}} \left[ \frac{1}{4} \sqrt{\frac{\pi}{B^3}} \right] \quad \therefore P = \frac{mn}{2B}$$

But from gas equation  $P = \frac{RT}{V} = \frac{NkT}{V}$

Where  $N$  is Avogadro's number,  $k$  is Boltzmann's constant

Because  $\frac{N}{V} = n$ ,  $P = nkT$   $\therefore \frac{mn}{2B} = nkT$

$$\therefore B = \frac{m}{2kT} \quad \dots\dots (7)$$

$$\therefore A = \left( \frac{B}{\pi} \right)^{\frac{1}{2}} = \left( \frac{m}{2\pi kT} \right)^{\frac{1}{2}} \quad \dots\dots (8)$$

Thus the Number of molecules having velocity components between  $u$  and  $(u + du)$  and  $v$  and  $(v + dv)$ ,  $w$  and  $(w + dw)$  is given by

$$dn = n f(u) f(v) f(w) du dv dw$$

$$\therefore dn = n \cdot A^3 e^{-\lambda/2(u^2 + v^2 + w^2)} du dv dw$$

$$dn = n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-m/2kT(u^2 + v^2 + w^2)} du dv dw \quad \dots\dots (9)$$

Maxwell's eqn. (9) represents Maxwell's distribution Law.

From this expression we can deduce the number of molecules having velocities lying between  $C$  and  $(C + dC)$ . Hence  $du dv dw$  represents an element of volume in the velocity space and its place, we must substitute the total volume in the velocity space lying between  $C$  and  $C + dC$ . In spherical polar coordinates the volume of the element becomes  $4\pi C^2 dC$ .

$$\therefore dn = 4\pi n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-mC^2/2kT} C^2 dC \quad \dots\dots (10)$$

This is the general expression for Maxwell's distribution velocities of molecules.

1. The different parts of the gas has different velocities. This will result in relative motion of the different layers of the gas with respect another. In such a case, the layers moving faster will impart momentum to the layers moving slower to bring about an equilibrium state. This transfer of momentum is known as "Viscosity".

2. The temperature of the gas may not be same through out. In such a case the molecules of a gas will carry kinetic energy from regions of higher temperature to the regions of low temperature to bring about an equilibrium state. This transfer of energy is known as "Conduction".

3. The different parts of the gas may have different molecular concentrations, in such a case the molecules of the gas will move from regions of higher concentrations to regions of lower concentration to bring about equilibrium state. This transport of molecules themselves is the phenomenon of diffusion. It is thus clear that viscosity, conduction and diffusion represents the transport of momentum, energy and mass respectively which are all grouped under the general term "Transport Phenomenon."

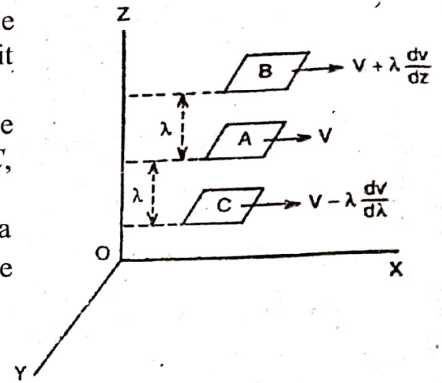


**Q. 2. Derive an expression for the coefficient of viscosity of a gas on the basis of Kinetic theory?**

**Ans :** a) Consider a gas in motion parallel to the horizontal plane (XY plane) and no motion along Z-axis. Let  $v$  be the velocity and it increases upwards as  $z$  increases.

Let  $v$  be the velocity of the molecules of gas in the layer A. The molecules in B, above A possess greater velocity and the molecules in C, below A possess smaller velocity.

We can consider every molecule, on the average to traverse a distance  $\lambda$  equal to the mean free path and then suffer a collision. If the velocity gradient is  $\frac{dv}{dz}$  along Z-axis the mean molecu



lar velocity of the molecules in B is  $\left(v + \lambda \frac{dv}{dz}\right)$  and in C is  $\left(v - \lambda \frac{dv}{dz}\right)$ . Due to thermal motion, on the average, the number of molecules along the Z-axis is one-third of the total number of molecules and only one sixth of the total number in the down ward or upward direction along Z-axis.

Consider the gas consisting of  $n$  molecules per unit volume possessing the mean velocity  $\bar{C}$ . The number of molecules crossing unit area per second in the upward direction is  $\frac{1}{6} n \bar{C}$  and this also equal to the number of molecules in a parallelopiped of unit face area and height  $\bar{C}$  is  $\bar{C} n$ .

The momentum transferred across the layer A due to the molecules going upward direction is  $\frac{1}{6} mn \bar{C} \left(v - \lambda \frac{dv}{dz}\right)$ . Similarly the momentum transferred across the layer A due to the molecules going downward is  $\frac{1}{6} mn \bar{C} \left(v + \lambda \frac{dv}{dz}\right)$  (since momentum = mass  $\times$  velocity)

Hence the total momentum transferred downwards on the

$$\begin{aligned} \text{layer A is } & \frac{1}{6} n \bar{C} m \left(v + \lambda \frac{dv}{dz}\right) - \frac{1}{6} n \bar{C} m \left(v - \lambda \frac{dv}{dz}\right) \\ &= \frac{2}{6} n \bar{C} m \lambda \frac{dv}{dz} = \frac{1}{3} n m \bar{C} \lambda \frac{dv}{dz} = \frac{1}{3} \rho \bar{C} \lambda \frac{dv}{dz} \end{aligned}$$

(Since  $mn = \rho$  density of the gas)

Since the change in momentum per second is the force acting, this change in momentum exert an accelerating force on the lower layers or the lower layers will return this faster layer by the same force.

From the definition of viscosity, retarding force =  $\eta \frac{dv}{dz}$  per unit area.

$$\text{Hence } \eta \frac{dv}{dz} = \frac{1}{3} \rho \bar{C} \lambda \frac{dv}{dz} \quad \therefore \eta = \frac{1}{3} \rho \bar{C} \lambda$$

b) As the temperature increases the coefficient of viscosity of the gas increases. This is because,

$$\bar{C} \propto \sqrt{T} \text{ and } \eta \propto \bar{C}$$

**Q. 3. Derive an expression for thermal conductivity of a gas on the basis of kinetic theory ?**

**Ans :** Consider the planes A, B, C parallel to the XOY plane and the distance between the planes A and B is  $\lambda$  and A and C is also  $\lambda$  where  $\lambda$  is the mean free path of the molecules

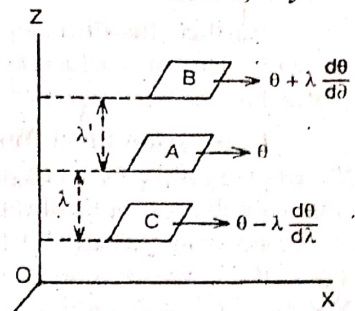


of the gas  $\frac{d\theta}{dz}$  is the temperature gradient along the Z-axis.

Hence the temperatures of molecules of the gas in the layers B

and C are  $\left(\theta + \lambda \frac{d\theta}{dz}\right)$  and  $\left(\theta - \lambda \frac{d\theta}{dz}\right)$  respectively.

Fig



Due to thermal motion of the molecules of the gas, the mass of the molecules crossing unit area of the layer A per second

in the upward direction or downward direction is  $\left(\frac{mn\bar{C}}{6}\right)$  where n is the number of molecules per

unit volume, m is the mass of molecule and  $\bar{C}$  is mean velocity of the molecules.

Quantity of heat carried by the molecules from B crossing unit area of A per second

$$= \left(\frac{mn\bar{C}}{6}\right) C_v \left(\theta + \lambda \frac{d\theta}{dz}\right) \quad \text{..... (1)}$$

( $C_v$  is the special heat constant volume of the gas)

Quantity of heat carried by the molecules from C crossing unit area of A per second

$$= \left(\frac{mn\bar{C}}{6}\right) C_v \left(\theta - \lambda \frac{d\theta}{dz}\right) \quad \text{..... (2)}$$

The net amount heat transferred per unit area of A per unit time is from hotter side to cooler side is

$$\begin{aligned} &= \left(\frac{mn\bar{C}}{6}\right) C_v \left(\theta + \lambda \frac{d\theta}{dz}\right) - \left(\frac{mn\bar{C}}{6}\right) C_v \left(\theta - \lambda \frac{d\theta}{dz}\right) \\ &= \left(\frac{2mn\bar{C}}{6}\right) C_v \left(\lambda \frac{d\theta}{dz}\right) = \frac{1}{3} \rho \bar{C} \lambda C_v \frac{d\theta}{dz} \quad \text{..... (3)} \end{aligned}$$

(Since  $mn = \rho$ )

From the definition of thermal conductivity the quantity of heat flowing per second across unit area

$$\text{is } Q = k.l. \frac{d\theta}{dz} \quad \text{..... (4)}$$

From (3) and (4) We have  $k.l. \frac{d\theta}{dz} = \frac{1}{3} \rho \bar{C} \lambda C_v \frac{d\theta}{dz}$

$$\therefore k = \frac{1}{3} \rho \bar{C} \lambda C_v$$

**Q. 4. Derive an expression for the coefficient of viscosity of a gas on the basis of Kinetic theory?**

**Ans :** Consider the case of two gases (say  $H_2$  and  $N_2$ ) at the same temperature and pressure. Let the two gases be brought in a vessel in such a way that the lighter gas  $H_2$  is in the upper part and heavier gas  $N_2$  is in lower part. It is observed that the heavier molecules of  $N_2$  move up while the lighter molecules of  $H_2$  move down till the gases become thoroughly mixed. This phenomenon is called as diffusion.

The diffusion is the process by which the mass gets transferred inside a gas from a region of higher concentration to a region of lower concentration.

Further, the diffusion coefficient ( $D$ ) of a gas is defined as the number of molecules of the gas crossing per unit surface area per second per unit concentration gradient. The phenomenon can be explained on the basis of kinetic theory of gases by considering the transport of the mass across a given plane.

**Expression for diffusion coefficient ( $D$ ):** Consider that a mass of the gas is moving between parallel planes AB and CD. Let the concentration (number of molecules per unit volume) increase in vertical direction as we go from AB to CD through the intermediate plane XY (see fig). Thus, the concentration of the gas above XY is greater than that below XY. In order to bring the equilibrium, the molecules of the gas will cross the plane XY from AB to CD and vice versa, due to thermal agitation. The phenomenon is known as diffusion. The diffusion of gas molecules through the intermediate plane can be considered as the transport of the mass.

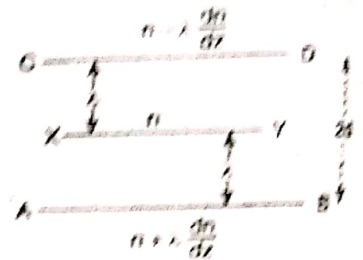


Fig.

Let  $n$  = concentration of gas molecules of plane XY.

$\frac{dn}{dz}$  = concentration gradient (rate of change of concentration in vertical direction).

Then, concentration at plane CD =  $n + \lambda \left( \frac{dn}{dz} \right)$ ,

where  $\lambda$  = distance between planes XY and CD. Here  $\lambda$  denotes the mean free path

Similarly, concentration at plane AB =  $n - \lambda \left( \frac{dn}{dz} \right)$

As the molecules are moving in all possible directions due to thermal agitation, we can take  $(1/3)$  of the total number move along any axis or  $(1/6)$  of molecules along any axis in one particular direction. The number of molecules crossing plane XY downwards per unit area per second will be

$$\frac{1}{6} \bar{C} \left( n + \lambda \frac{dn}{dz} \right)$$

and those upward will be  $\frac{1}{6} \bar{C} \left( n - \lambda \frac{dn}{dz} \right)$

So, the net number crossing unit area per second of plane XY in downward direction is

$$\frac{1}{6} \bar{C} \left( n + \lambda \frac{dn}{dz} \right) - \frac{1}{6} \bar{C} \left( n - \lambda \frac{dn}{dz} \right) = \frac{1}{3} \bar{C} \lambda \frac{dn}{dz}$$

Now, the coefficient  $D$  is given by

$$D = \frac{\text{No. of molecules crossing unit area per sec}}{\text{Concentration gradient}}$$

$$= \frac{\frac{1}{3} \bar{C} \lambda \frac{dn}{dz}}{\frac{dn}{dz}} = \frac{1}{3} \bar{C} \lambda \quad \text{or} \quad D = \frac{1}{3} \bar{C} \lambda$$

Now,  $D = \frac{1}{3} \frac{\bar{C} \lambda p}{\rho} = \frac{\eta}{\rho}$  where  $\eta = \frac{1}{3} \bar{C} \lambda p$  = coefficient of viscosity.

$$D = \frac{\eta}{\rho}$$



For  $\lambda \propto \frac{1}{n} \propto \frac{T}{p} \propto \sqrt{T}$ , hence

$$D = T^{3/2} p^{-1}.$$

**Conclusion :** Thus, the coefficient of diffusion is directly proportional to  $T^{3/2}$ , where  $T$  is the absolute temperature and is inversely proportional to pressure  $p$ .

### SHORT ANSWER QUESTIONS

**Q. 1. Derive the toothed wheel experiment to verify the Maxwell's law of distribution of molecular speeds.**

**Ans :** In the year 1920, Stern verified Maxwell's speed distribution law experimental arrangement,  $O$  is an oven which  $Hg$  is evaporated. And the  $Hg$  atoms pass through the slits  $S_1$ ,  $S_2$  and two wheels  $A, B$ . These wheel are arranged on the same axis at a distance,  $x$ . On the edge of each wheel there are 50 slots. The slots in  $B$  are not exactly parallel to the slots in  $A$ , but are inclined at an angle at an angle  $2^\circ$ .

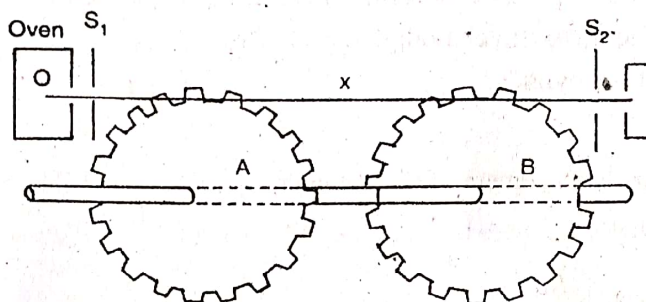


Fig.

The beam of  $Hg$  molecules passes through  $S_1$  towards  $S_2$  through slots in  $A$  and  $B$  and then strike the glass plate  $P$ .

The principle of the experiment is based on the fact that these molecules are able to pass through a slot in  $B$  which have the requisite speed to cover the distance ' $x$ ' in the interval of time taken by the wheel to turn through an angle of  $2^\circ$ . These molecules deposited on the plate  $P$ . By rotating the wheels with various speeds, the molecules of different speeds can be separated. By measuring relative densities, the relative number of molecules lying in different ranges are calculated. It is found that the distribution of speeds is in accordance with Maxwell's law.

**Q. 2. Describe the experimental methods to verify the Maxwell's law of distribution of molecular speeds.**

**Ans :** It is observed from the graph that it resembles with the theoretical curve for Maxwell's distribution law of molecular speeds.

**Estermann, Simpson and Stern Method :** In 1947 Estermann, Simpson and Stern designed a more precise apparatus to study the velocity distribution as shown in fig.

Cesium atoms from the oven emerge from the opening  $A$ . After passing through the slit  $S$ , they fall on a hot tungsten wire  $P$ . The tungsten wire is placed in a negatively charged cylinder which can be moved into different positions along the tungsten wire. The entire arrangement is enclosed in an almost evacuated chamber.

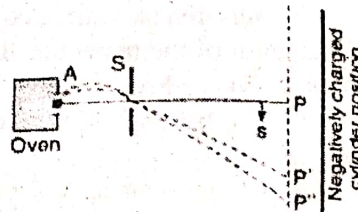


Fig.

In the absence of downward gravitational pull, the cesium atoms strike the wire at  $P$ . But due to gravitational pull, the atoms travel along parabolic path. The faster moving atoms meet the wire at  $P'$  while slower one at  $P''$ . The slowest atom fails to reach the wire.

When cesium atoms strike the wire, they get ionised and re-evaporate. They are collected by the negatively charged detecting cylinder. The magnitude of the current indicates the intensity of the atoms. The cylinder is moved to different positions and the ionising current is measured. This gives the number of atoms striking the wire at different points.



The vertical heights on the detecting cylinder at which the atoms strike the cylinder correspond to the velocity of the atoms reaching there. A graph is then drawn between ionisation current along Y-axis and the vertical height  $s$  (speed of atoms) of the detector along the X-axis. The velocity distribution is found to be in agreement with the Maxwellian distribution is found to be in agreement with the Maxwellian distribution law of velocities.

**Miller and Kusch Method :** The Miller and Kusch apparatus (fig) consists of an oven  $O$  in which thallium vapour is filled. The molecules of the vapour come out at the oven through slit  $S$ . Then they fall on a rotating cylinder  $R$  which has a number of helical grooves cut into its body. Finally the molecules come to a detector  $D$  where their intensity is recorded. The apparatus is kept in high vacuum chamber.

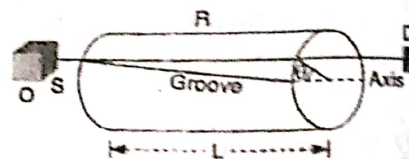


Fig.

Here the rotating cylinder acts as a velocity selector. At a particular angular speed, the molecules having a definite speed can only pass through the grooves and reach the detector. Let  $\omega$  be the angular speed of the cylinder and  $v$  be the speed of molecules that could reach the detector. Now

$$\text{Time taken by the molecule to travel along the groove } t = l/v \quad \dots(1)$$

where  $l$  is the length of the cylinder.

$$\text{Further, } t = \theta / \omega$$

$$\text{where } \theta \text{ is the angular displacement of the cylinder} \quad \dots(2)$$

From eqs. (1) and (2),

$$\frac{l}{v} = \frac{\theta}{\omega} \quad \text{or } v = \frac{l\omega}{\theta} \quad \dots(3)$$

The angular speed of the cylinder is adjusted such that molecules of different velocities are made to pass through the grooves. They then strike the cylinder. The intensity of the beam of molecules (recorded by detector) depends on the speed  $v$  selected by a groove. In this way, the number of molecules at a particular velocity is given by the intensity of molecules recorded by detector. It is observed that the velocity distribution is found to be in agreement with Maxwell's distribution law.

**Q. 3. Write the postulates of kinetic theory of gases.**

- Ans :**
1. All gases contain tiny, rigid, spherically shaped particles known as Molecules.
  2. The molecules are in random motion with different velocities ranging from zero to infinity.
  3. The molecules are colliding with the walls of the vessel and with the other molecules.
  4. The molecules are perfectly elastic and there are no inter molecular forces of attractions or repulsions.
  5. As the temperature increases the velocity of the molecules increases.
  6. The average kinetic energy of the gas molecules is directly proportional to the absolute temperature of the gas.
  7. Between two successive collisions, a molecule moves in a straight line. This distance is called the free path of the molecule. The average distance travelled by a molecule between the two collisions is known as Mean Free Path.
  8. The time spent at a collision is neglected in comparison with the time taken to travel the mean free path.
  9. The number of molecules per c.c. of the gases is very large and remains constant in the space.

From kinetic theory of gases, we can write

$$PV = \frac{1}{3} mn \bar{C}^2$$

$V$  = Volume containing 'n' number of molecules

$m$  = mass of each molecule

$\bar{C}^2$  = mean square speed of molecules

$$\text{But } \bar{C}_{Rms} = \sqrt{\bar{C}^2} = \sqrt{\frac{3kT}{m}}$$

According to law of equilibration of energy the total energy of a molecule is equally divided among its degree of freedom. In translation motion, the molecule has three degrees of freedom.

$$\text{Average K.E. per degree of freedom} = \frac{1}{2} kT$$

**Q. 4. Write a brief note on Mean free path and Degrees of freedom ?**

**Ans :** According to kinetic theory of gases, the molecules of a gas are continuously moving with large velocities. They collide with each other. At each collision the speed as well as direction changes. Between two successive collisions, the molecule moves in a straight line. This distance is called as free path. Let  $a, b, c, d, \dots$  be the *free paths* i.e., distances travelled by a molecule between successive collisions. Then average distance  $\lambda$  travelled between two collisions is

$$\lambda = \frac{a + b + c + d + \dots}{n}$$

where  $n$  is the number of collisions suffered by the molecule and  $\lambda$  is known as mean free path.

Thus, the mean free path is defined as the average distance travelled by a molecule between two successive collisions.

**Expression for mean free path :** For the simplicity of calculation, it is assumed that

(i) Only one molecule under consideration is in motion while all other molecules of the gas are at rest.

(ii) The molecule under investigation will collide with all those molecules whose centres lie within a distance  $d$  from its centre as shown in fig (8). Alternately, we may describe the collision by regarding the moving molecule of diameter  $2d$  and all other molecules as point particles.

Let us now think that a molecule of equivalent diameter  $2d$  is moving with speed  $v$  through a gas of molecules assumed to be point spheres.

It is assumed here that only this molecule is under consideration and other point spheres of the gas exert no force on each other. Now in time  $t$ , the moving molecule will sweep out a cylinder of length  $vt$  and cross-sectional area  $\pi d^2$  as shown in fig. Moreover, in time  $t$  this molecule will collide with all the molecules whose centres lie within the cylinder whose axis is the line of motion of its centre and radius  $d$  as shown in fig.

The volume of the cylinder =  $\pi d^2 vt$

The number of molecules in the cylinder =  $\pi d^2 vt n$

(when  $n$  is the number of molecules per unit volume)

(number of collisions made by the molecules in one second

$$= \pi d^2 v n$$

Hence the average time between two successive collisions

$$= \frac{1}{\pi d^2 v n}$$

So the average distance between two successive collisions

$$= \frac{\text{distance covered in one second}}{\text{number of collisions made per second}} = \frac{1}{\pi d^2 v n} = \frac{1}{\pi d^2 n}$$

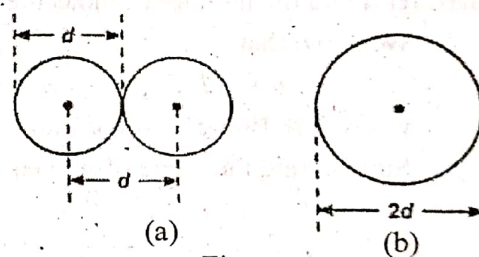
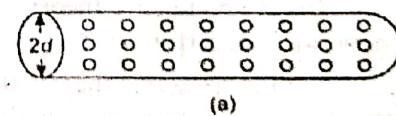
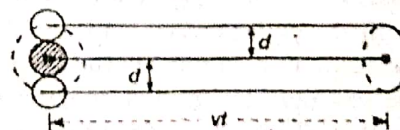


Fig.



(a)



(b)

Fig.



$$\text{Mean free path, } \lambda = \frac{1}{\pi d^2 n}$$

If  $m$  be the mass of the molecule, then  $m n = \rho$ , the density of the gas. Thus the expression for mean free path in terms of density becomes

$$\lambda = \frac{m}{\pi d^2 \rho}$$

Here  $(m/\pi d^2)$  is a constant, hence  $\lambda \propto 1/\rho$

This expression shows that mean free path is inversely proportional to the density of the gas. We also know that the density of a gas varies directly as the pressure and inversely as the absolute temperature. Thus the mean free path varies directly with absolute temperature and inversely as the pressure.

Boltzmann on the consideration that all the molecules travel with the same average speed in all possible directions, obtain an expression

$$\lambda = \frac{3}{4 \pi d^2 n} \quad \dots(2)$$

Maxwell improved the above result by considering the distribution of molecular speeds and obtained the result

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n}$$

Eq. (3) shows that the mean free path of a molecule is inversely proportional to the square of the diameter  $d$  and the number of molecules  $n$  per unit volume i.e., the density of gas

We know that

$$p = n k T \quad \text{or} \quad n = p / k T$$

where  $k$  is Boltzmann constant.

Substituting the value of  $n$  in eq. (3), we get

$$\lambda = \frac{k T}{\sqrt{2} \pi d^2 p}$$

This expression shows that mean free path  $\lambda$  is *inversely proportional to the pressure of the gas and directly proportional to the absolute temperature.*

#### **Q. 5. What do you mean by Transport Phenomenon ?**

**Ans :** The kinetic theory of gases explains satisfactorily the observed phenomenon like viscosity, conduction and diffusion.

According to this theory, the molecules of a gas are in a state of thermal agitation. Each molecule possesses mass, momentum and energy which it carries with in itself as it moves about in the gas. On collision with another molecule, it transfers either the momentum or energy to the latter. This second molecule in turn repeats the same as it collides with the third molecule and so on. Thus the molecules of the gas may be treated as carriers or transporters of mass, momentum or energy from one region to another through a series of successive collisions.

If the gas were in a steady-state, transport of any these physical quantities in one direction is just balanced by an equal transport of same quantity in the reverse direction and there would be no net transport. But in the non-equilibrium state of a gas, there may be a large concentration of either energy or momentum in one region of the gas. Molecules transport the quantity concerned from the former to the latter region through a long chain of collisions.

1. The different parts of the gas has different velocities. This will result in relative motion of the



different layers of the gas with respect another. In such a case, the layers moving faster will impart momentum to the layers moving slower to bring about an equilibrium state. This transfer of momentum is known as "Viscosity".

2. The temperature of the gas may not be same through out. In such a case the molecules of a gas will carry kinetic energy from regions of higher temperature to the regions of low temperature to bring about an equilibrium state. This transfer of energy is known as "Conduction".

3. The different parts of the gas may have different molecular concentrations, in such a case the molecules of the gas will move from regions of higher concentrations to regions of lower concentration to bring about equilibrium state. This transport of molecules themselves is the phenomenon of diffusion. It is thus clear that viscosity, conduction and diffusion represents the transport of momentum, energy and mass respectively which are all grouped under the general term "Transport Phenomenon."

**Q. 6. Obtain the relation between viscosity ( $\eta$ ) and thermal conductivity ( $k$ ) of gases.**

**Ans :** The relation between thermal conductivity and viscosity is expressed as

The coefficient of viscosity of gases expressed as

$$\eta = \frac{1}{3} \rho \bar{C} \lambda$$

and the coefficient of thermal conductivity of gases expressed as

$$K = \frac{1}{3} \rho \bar{C} C_v \lambda$$

in place of  $\frac{1}{3} \rho \bar{C} \lambda$  put  $\eta$  in eq (2) we get

$$k = \frac{1}{3} \rho \bar{C} \lambda \cdot C_v \quad K = \eta C_v$$

$$\therefore \frac{k}{\eta} = C_v \quad (\text{or}) \quad \frac{\eta}{K} = \frac{1}{C_v}$$

#### SOLVED PROBLEMS

**Q. 1. Calculate the mean free path of hydrogen molecules given that the diameter of the molecules =  $3 \times 10^{-10} \text{ m}$ . At standard pressure of 760 mm of Hg a mole of the gas has  $6 \times 10^{23}$  molecules and occupies  $22.4 \times 10^3 \text{ m}^3$ .**

**Sol :**  $d = 3 \times 10^{-10} \text{ m}$

$$n = \frac{6 \times 10^{23}}{22.4 \times 10^{-23}} \text{ molecules / m}^3$$

$$\lambda = \frac{1}{\sqrt{2} n d^2} = \frac{22.4 \times 10^{-3}}{2 \times 6 \times 10^{23} \times 9 \times 10^{-20}}$$

$$\lambda = 9 \times 10^{-8} = \text{m (nearly)}$$

**Q. 2. Find the mean free molecular path in air given the density of air =  $1.2 \times 10^{-3} \text{ gm/cm}^3$  at  $0^\circ \text{C}$  and the pressure of  $10^6 \text{ dynes/Sq. cm}$  and its coefficient of viscosity  $\eta = 1.7 \times 10^{-4} \text{ dynes / Sq. cm per unvelocity gradient}$ .**

**Sol :** Since  $\eta = \frac{1}{3} \rho \bar{C} \lambda$

$$\therefore \lambda = \frac{3\eta}{\rho \bar{C}}$$

$$\text{From } \bar{C} = \sqrt{\frac{3P}{\rho}}$$

$$\text{Hence, } \lambda = \frac{3\eta}{\rho \sqrt{\frac{3P}{\rho}}} = \eta \sqrt{\frac{3}{P\rho}}$$

$$\lambda = 1.7 \times 10^{-3} \times \sqrt{\frac{3}{10^6 \times 1.2 \times 10^3}} = 8.498 \times 10^{-6} \text{ cm}$$

**Q. 3.** Find the mean free path of molecules of air, taken as uniform gas. Given  $r = 1.2 \text{ kg m}^{-3}$  at  $0^\circ\text{C}$  and a pressure of  $10^5$  Newtons  $\text{m}^{-2}$  and  $\eta = 1.7 \times 10^{-5}$  Newtons  $\text{m}^{-2}$  per unit velocity gradient.

$$\text{Sol : i) } \rho = \frac{1}{3} \rho \bar{C}^2$$

$$\text{ii) } \eta = \frac{1}{3} \rho \bar{C} \lambda$$

$$\therefore \eta = \frac{1}{3} \rho \lambda \sqrt{3P/\rho} = \lambda \sqrt{P\rho/3} \quad \text{or } \lambda = \eta \sqrt{\frac{3}{P\rho}}$$

Substituting value given

$$\lambda = 1.7 \times 10^{-5} \frac{3}{10^5 \times 1.2} = 8.498 \times 10^{-8} \text{ m}$$

**Q. 4.** The viscosity of argon gas at N.T.P is  $2.1 \times 10^{-5}$  Newton sec  $\text{m}^{-2}$  Argon is monatomic gas with a molecular weight of 40. What is its mean free path and collision frequency?

**Sol :** We know

$$\text{i) } \eta = \frac{1}{3} \rho \bar{C} \lambda \quad \text{or } \lambda = 3\eta / \rho \bar{C}$$

$$\text{but } \rho = \frac{40}{22.4} = \frac{1000}{560} \text{ kgm}^{-3}$$

If  $m$  be the mass of one molecule of the gas we have  $m = \frac{M}{N}$

$$\text{and K.E. of one molecule of gas} = \frac{1}{2} m \bar{C}^2 = \frac{1}{2} \frac{M}{N} \bar{C}^2$$

$$\text{But K.E.} = \frac{3}{2} kT$$

$$\frac{1}{2} \frac{M}{N} \bar{C}^2 = \frac{3}{2} kT$$

$$\bar{C}^2 = \frac{3N}{M} kT$$

$$\bar{C} = \sqrt{\frac{3NkT}{M}} = 4.118 \times 10^2 \text{ m sec}^{-1}$$

$$\therefore \lambda = \frac{3\eta}{\rho \bar{C}}$$

$$\therefore \lambda = \frac{3 \times 2.1 \times 10^{-5}}{\frac{1000}{560} \times 411.8 \times 10^2} = 8.567 \times 10^{-8} \text{ m}$$

$$f = \frac{\bar{C}}{\lambda} = \frac{411.8}{8.567 \times 10^{-8}} = 4.8 \times 10^9 \text{ Hz}$$

- Q. 5.** The coefficient of viscosity of Nitrogen at S.T.P. is  $66 \times 10^{-6}$  poise and density  $1.25 \text{ kg m}^{-3}$  and average speed of the molecule  $450 \text{ ms}^{-1}$  and molecular density  $n$  is  $2.7 \times 10^{25} \text{ m}^{-3}$ . Find the mean free path and diameter of molecule.

**Sol :** a) We know mean free path  $\lambda = \frac{3\eta}{\rho c}$

Coefficient of viscosity of Nitrogen at S.T.P  $16.6 \times 10^{-6}$  poise

$$\lambda = \frac{3 \times 16.6 \times 10^{-6}}{1.25 \times 450} \times 8.853 \times 10^{-8} \text{ m}$$

b) Diameter of the molecule  $d = \sqrt{\left(\frac{1}{\sqrt{2}\pi n\lambda}\right)}$

Molecular density  $n = 2.7 \times 10^{25}$

$$d = \sqrt{\frac{1}{\sqrt{2} \times 3.141 \times 2.7 \times 10^{25} \times 8.853 \times 10^{-8}}}$$

$$= 3.069 \times 10^{-6} \text{ m}$$

- Q. 6.** The mean free path of nitrogen molecules at  $0^\circ\text{C}$  and 1 atmosphere is  $0.8 \times 10^{-5} \text{ cm}$ . At this temperature and pressure there are  $2.7 \times 10^{19}$  molecules / c.c. Calculate the molecular diameter ?

**Sol :** Here,  $\lambda = 0.8 \times 10^{-5} \text{ cm}$ ,  $n = 2.7 \times 10^{19}$ ,  $d = ?$

We know  $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$  (or)  $d^2 = \frac{1}{\sqrt{2}\pi \lambda n}$

$$\text{or } d = \sqrt{\left(\frac{1}{\sqrt{2}\pi n\lambda}\right)} = \sqrt{\left(\frac{1}{\sqrt{2} \times \pi \times 2.7 \times 10^{19} \times 0.8 \times 10^{-5}}\right)}$$

$$\therefore d = 3.228 \times 10^{-8} \text{ cm}$$

- Q. 7.** Calculate the mean free path of Nitrogen molecules given that at N.T.P the coefficient of viscosity is  $166 \times 10^{-6} \text{ dynes / cm}^2 / \text{unit velocity gradient}$ , average molecular speed is  $4.5 \times 10^4 \text{ cm/sec}$ . molecular weight of Nitrogen is 28 ?

**Sol :** Here,  $\eta = 1.66 \times 10^{-6}$ ,  $\bar{C} = 4.5 \times 10^4 \text{ cm/sec}$   
dyne/cm<sup>2</sup>/unit velocity gradient

$$\therefore \text{Density of the nitrogen } \rho = \frac{28}{22.4} = 12.5 \times 10^{-3}$$

But,  $\eta = \frac{1}{3} \rho \bar{C} \lambda$  or  $\lambda = \frac{3\eta}{\rho \bar{C}}$

$$\text{So, } \lambda = \left(\frac{3 \times 166 \times 10^{-6}}{1.25 \times 10^{-3} \times 4.5 \times 10^4}\right)$$

$$\lambda = 8.853 \times 10^{-6} \text{ cm}$$

—O—



## UNIT - II

# THERMODYNAMICS

### LONG ANSWER QUESTIONS

**Q. 1. What are Isothermal and Adiabatic processes? Derive the expression for work done in isothermal and Adiabatic processes?**

**Ans : Isothermal and Adiabatic Change :**

**Isothermal Change :** Isothermal change is the process that takes place at constant temperature. The system is in thermal equilibrium with its surrounding throughout the isothermal change. For example a gas in a cylinder is in contact with a constant temperature enclosure can be compressed slowly by lowering the piston. The work done on the gas appears in the form of heat energy and heat flows into the surroundings keeping the temperature of the gas constant. Similarly when the gas in the cylinder is allowed to expand the work done by the gas is at the expense of heat energy of the gas and heat flows from the surroundings to the gas, keeping the temperature of the gas constant. Hence the isothermal change is slow compression and expansion of the gas keeping its temperature constant. In this process heat flows from the gas to the surroundings and vice versa. This change is represented by the equation  $PV = \text{constant}$  at constant temperature.

**Adiabatic Change :** Adiabatic change is the process during which no energy enter or leaves the system. In an adiabatic expansion of a gas, mechanical work is done by the gas as its volume increases and the temperature of the gas falls. For an ideal gas undergoing adiabatic changes it can be shown that

$$PV^\gamma = \text{Constant}$$

$$T^\gamma P^{1-\gamma} = \text{Constant}$$

$TV^{\gamma-1} = \text{Constant}$  where  $\gamma$  is the ratio of the specific heats of a gas i.e.,

$$\gamma = \frac{C_p}{C_v}$$

**Work done by a gas during an Isothermal process :** Consider a gram molecule of a perfect gas undergoing an isothermal change. Let  $dV$  be the expansion produced (at constant temperature) against a pressure  $P$ . Then  $dW$  the work done is given by

$$dW = P dV$$

Let  $P_1$  and  $V_1$  represents the initial condition of the gas and  $P_2$  and  $V_2$  the final condition after isothermal expansion. Hence  $W$  the total work done is given by

$$W = \int_{V_1}^{V_2} P dV$$

$$\text{But } PV = RT \text{ or } P = \left[ \frac{RT}{V} \right]$$

$$\therefore dW = \int_{V_1}^{V_2} \frac{RT}{V} dV = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

Since  $R$  is constant and  $T$  also a constant during an isothermal process

$$\text{Hence } W = RT(\log_e V)_{V_1}^{V_2} = RT \log_e \frac{V_2}{V_1} \quad \left[ \therefore \log_e \frac{V_2}{V_1} = 2.3026 \log_{10} \left( \frac{V_2}{V_1} \right) \right]$$

$$W = 2.3026 RT n \log_{10} \frac{V_2}{V_1}$$

$$\text{or } W = 2.3026 RT n \log_{10} \left( \frac{P_1}{P_2} \right) \left( \because \frac{P_1}{P_2} = \frac{V_2}{V_1} \right)$$

**Work done by a gas during an Adiabatic process :** During an adiabatic process the system is thermally insulated so that heat is allowed to either enter or leave the system as a result of which the heat content of the system does not remain constant during the process. Hence the temperature may either rise or fall.

Consider a gram molecule of a perfect gas under going an adiabatic change. Let  $dV$  be the expansion produced against a pressure  $P$ . Then  $dW$  the work done is given by

$$dW = P.dV$$

Let  $P_1$  and  $V_1$  represents the initial condition of the gas and  $P_2$  and  $V_2$  the final condition after adiabatic expansion. Hence the  $W$  the total work done is given by,

$$W = \int_{V_1}^{V_2} P.dV$$

$$\text{But } PV = K \text{ or } P = \frac{K}{V^\gamma}$$

$$\therefore W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV = K \left[ \frac{V^{1-\gamma}}{1-\gamma} \right]_{V_1}^{V_2}$$

$$\therefore W = K \left[ \frac{V_2^{1-\gamma}}{1-\gamma} - \frac{V_1^{1-\gamma}}{1-\gamma} \right]$$

$$\therefore W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV \therefore W = K \left[ \frac{V_2^{1-\gamma}}{1-\gamma} - \frac{V_1^{1-\gamma}}{1-\gamma} \right] = \frac{1}{1-\gamma} [KV_2^{1-\gamma} - KV_1^{1-\gamma}]$$

$$\text{But } P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

$$\therefore W = \left[ \frac{1}{1-\gamma} \right] [P_2 V_2^\gamma \cdot V_2^{1-\gamma} - P_1 V_1^\gamma \cdot V_1^{1-\gamma}] = \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1]$$

If the temperature of the gas changes from  $T_1$  to  $T_2$  during the process then

$$P_1 V_1 = RT_1 \text{ and } P_2 V_2 = RT_2$$

$$\therefore W = \frac{1}{\gamma-1} (RT_1 - RT_2) = \frac{R}{\gamma-1} (T_1 - T_2)$$

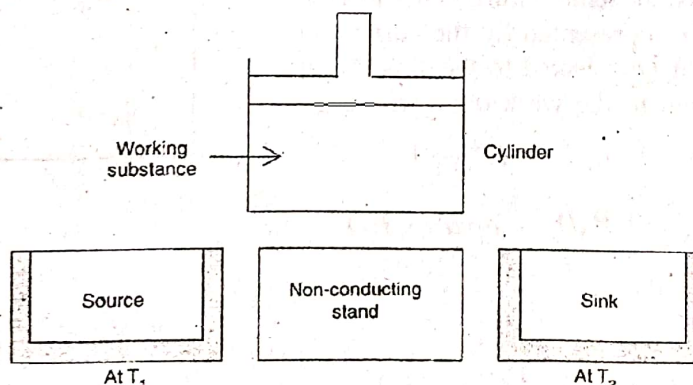
$$\therefore W = \frac{R}{\gamma-1} (T_1 - T_2)$$

**Q. 2. Describe the working of Carnot's Reversible Engine and derive an expression for its efficiency ?**

**Ans :** A heat engine is a device which converts heat continuously into mechanical work by absorbing heat from a hot body.

Carnot designed an ideal and simple heat engine (which can not be realised in practice) having the maximum efficiency. The ideal engine consists of :

1. A cylinder with perfectly non-conducting walls and perfectly conducting base. It is fitted with a perfectly non-conducting frictionless piston. The cylinder contains a perfect gas as the working substance.



**Fig.**



2. A hot body of infinite thermal capacity maintained at a constant high temperature  $T_1^0$  A serves as the source.
3. A cold body of infinite thermal capacity maintained at a constant lower temperature  $T_2^0$  A serves as the sink.
4. A perfectly non-conducting platform to serve as a stand for the cylinder.

**Carnot's cycle :** The working substance is supposed to undergo the following four operations, known as the Carnot's Cycle as shown in the Fig. Let the initial temperature of the gas in the cylinder be  $T_1^0$  A as that of the source and its state be represented by the point A on the  $PV$  indicator diagram.

1. The cylinder is placed on source and the piston is moved slowly so that the gas expands. As the gas expands, the temperature tends to fall, Hence heat is absorbed from the source at constant temperature  $T_1$ . The operation is performed very slowly so that the temperature of the gas is always  $T_1$ . This process is isothermal and is represented by one curve  $AB$  on the indicator diagram.

The amount of heat  $Q_1$  absorbed from the source is equal to the work done  $W_1$  by the gas in free expansion from a pressure  $P_1$  and volume  $V_1$  at A to a pressure  $P_2$  and volume  $V_2$  at B.

$$Q_1 = W_1 = \int_{V_1}^{V_2} P.dV = \text{area } ABEF = RT_1 \log_e \left( \frac{V_2}{V_1} \right) \quad \dots (1)$$

2. The cylinder is transferred from the source to the non-conducting stand. Now the gas is allowed to expand further, adiabatically. Since no heat is supplied, its temperature falls. The expansion is continued until the temperature falls to  $T_2^0$  A, the temperature of the sink. This expansion of the gas is represented by the adiabatic  $BC$ . Let  $P_3$  and  $V_3$  be the pressure and volume of the gas at C. The work done  $W_2$  by the gas is given by,

$$W_2 = \int_{V_2}^{V_3} P.dV = \text{area } BCGE = \frac{R}{(\gamma - 1)} (T_1 - T_2) \quad \dots (2)$$

Since the pressure of the gas is now very much reduced, it has lost its expansive power. Hence in order to recover its original capacity for doing work, it must be brought back to original conditions. This is achieved in two stages by compressing the gas first is thermally and then adiabatically as follows :

3. During the isothermal compression, the cylinder shifted from the insulated stand to the sink at  $T_2^0$  A. The piston is moved very slowly so that the gas is compressed until its pressure and volume become  $P_4$  and  $V_4$ . The heat which is developed during compression will now pass to the sink so that the change takes place at constant temperature. This isothermal compression is represented by the curve  $CD$ . The amount of heat  $Q_2$  rejected to the sink during this process is equal to the work done on the gas and is given by

$$Q_2 = W_3 = \int_{V_3}^{V_4} P.dV = \text{area } CGHD$$

$$= RT_2 \log_e \left( \frac{V_3}{V_4} \right) \quad \dots (3)$$

4. The cylinder is removed from the sink and placed again on the insulated stand. The gas is further compressed adiabatically. Since no heat rejected by the substance, its temperature rises. This

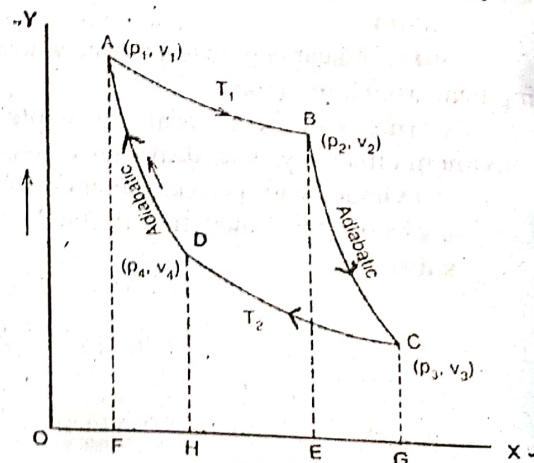


Fig.

process is continued until the temperature rise to  $T_1^0$  A (The temperature of the source) and the gas attains its original pressure  $P_1$  and volume  $V_1$ . The work done  $W_4$  on the gas during adiabatic cooperations is given by,

$$W_4 = \int_{V_2}^{V_1} P.dV = \text{area ADHF} \cdot \frac{R}{(\gamma-1)} (T_1 - T_2)$$

From eqn (2) and (4) it is clear that  $W_2 = W_4$

$\therefore$  Network done by the gas  $= W_1 + W_2 - W_3 - W_4 = W_2 - W_3 = \text{area ABCD}$

$\therefore$  The net amount of heat absorbed by the gas in units of work  $= Q_1 - Q_2$

**Calculation of efficiency of engine :** The efficiency of a heat engine is defined as the ratio of the external work done in one cycle to the corresponding amount of heat taken in from the source.

The efficiency  $\eta$  of the engine is given by

$$\eta = \frac{\text{Amount of heat converted to work}}{\text{Amount of heat drawn from the source}}$$

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

The efficiency  $\eta$  can also be expressed in terms of the temperature of the source and sink. We know that,

$$Q_1 - Q_2 = W_1 - W_3 = RT_1 \log_e \left( \frac{V_2}{V_1} \right) - RT_2 \log_e \left( \frac{V_3}{V_4} \right) = R \left[ T_1 \log_e \left( \frac{V_2}{V_1} \right) - T_2 \log_e \left( \frac{V_3}{V_4} \right) \right]$$

Since the point B and C lie on the same adiabatic

$$P_2 V_2^\gamma = P_3 V_3^\gamma$$

Similarly the points D and A lie on the same adiabatic

$$P_4 V_4^\gamma = P_1 V_1^\gamma$$

Since the points A and B lie on the same isothermal at  $T_1$

$$P_1 V_1 = P_2 V_2$$

Similarly the points C and D lie on the same isothermal at  $T_2$

$$P_3 V_3 = P_4 V_4$$

Multiplying the equations (6), (7), (8) and (9) we have

$$(P_1 P_2 P_3 P_4) (V_1 V_2^\gamma V_3 V_4^\gamma) = (P_1 P_2 P_3 P_4) (V_1^\gamma \cdot V_2 \cdot V_3^\gamma \cdot V_4)$$

$$\text{i.e., } V_2^{\gamma-1} V_4^{\gamma-1} = V_1^{\gamma-1} V_3^{\gamma-1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Substituting this value in Eqn., (5) we have

$$Q_1 - Q_2 = R \left[ T_1 \log \frac{V_2}{V_1} - T_2 \log \frac{V_2}{V_1} \right] \quad Q_1 - Q_2 = R \log (V_2 - V_1) (T_1 - T_2)$$

$$\therefore \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{R \log_e \left( \frac{V_2}{V_1} \right) (T_1 - T_2)}{RT_1 \log_e \left( \frac{V_2}{V_1} \right)} = \frac{(T_1 - T_2)}{T_1} = 1 - \frac{T_2}{T_1}$$

$$\text{Hence } \therefore \eta = 1 - \frac{T_2}{T_1} \text{ and } \eta = 1 - \frac{Q_2}{Q_1}$$

$$\text{or } \therefore \eta = 1 - \frac{Q_2}{Q_1} \text{ and } \eta = 1 - \frac{Q_2}{Q_1} \therefore \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$



$$\text{or } \frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

This equation shows that the efficiency depends only on temperature of the source and the sink and is always less than unity.

**Q. 3. State and prove Carnot's theorem.**

**Ans : Statement :** (a) No engine can be more efficient than a reversible engine working between the same two temperatures. (or)

All reversible engines working between the same two temperatures have the same efficiency.

**Explanation :** (a)  $R$  is the reversible heat engine and  $S$  is the irreversible heat engine and these two are coupled. These two engines work between the temperatures  $T_1$  K and  $T_2$  K.  $S$  works in the direct process and  $R$  works in the indirect process.

$S$  absorbs  $Q_1$  from the source, rejects  $Q_2$  to the sink and converts  $Q_1 - Q_2$  into mechanical energy. This mechanical energy is supplied to  $R$ .

$R$  absorbs  $Q_2'$  and rejects  $Q_1'$  and receives the energy  $(Q_1 - Q_2)$  from  $S$ .

$$\text{Hence } Q_1 - Q_2 = Q_1' - Q_2' \quad \dots(1)$$

Let the efficiency of  $S$  is  $\eta_s$  and that of  $R$  is  $\eta_R$  and let us assume  $\eta_s > \eta_R$

$$\eta_s = \frac{Q_1 - Q_2}{Q_1}; \eta_R = \frac{Q_1' - Q_2'}{Q_1'}$$

Since  $\eta_s > \eta_R$

$$\therefore \frac{Q_1 - Q_2}{Q_1} > \frac{Q_1' - Q_2'}{Q_1'} \quad \text{and as } Q_1 - Q_2 = Q_1' - Q_2' \quad \therefore \frac{1}{Q_1} > \frac{1}{Q_1'}; \therefore Q_1' < Q_1$$

From equations (1) and (2)  $Q_2' - Q_2 = Q_1 - Q_1'$  (positive)

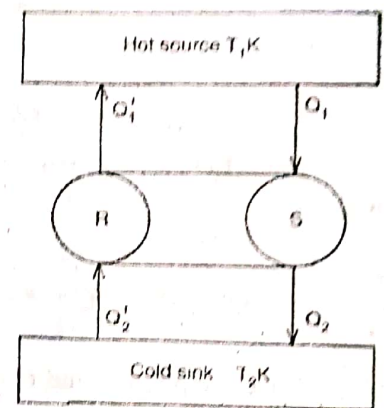
$$Q_2' - Q_2 = Q_1 - Q_1' \quad (\text{Positive quantities})$$

Hence the heat is transferred from the cold body to the hot body without the aid of the external agency. This is contrary to the second law of thermodynamics. Hence the efficiency  $\eta_s$  of irreversible engine can not be more than  $\eta_R$ . This proves the first part of the theorem.

(b) To prove the second part of the theorem let us consider the two engines  $R$  and  $S$  to be both reversible and suppose that  $R$  is more efficient than  $S$ . As explained as above  $\eta_s$  cannot be more than  $\eta_R$ . Thus it can be proved that the efficiency of all the reversible heat engines working between the same two temperatures is same.

**Q. 4. What is Entropy - Temperature (T-S) diagram ? What are its uses ? Obtain expression for the efficiency of a Carnot's engine using the entropy - temperature diagram ?**

**Ans :** The temperature and entropy of a substance form a pair with each other like pressure and volume. So that the values of  $S$  and  $T$  for the substance or system completely specify its thermodynamic state. Willard Gibbs was the first to suggest that the changes in the entropy of a given of a given substance or system undergoing a reversible process may be represented on a Temperature Entropy or  $T$ - $S$  diagram exactly like the changes in volume on an indicator ( $P$ - $V$ ) diagram. Such  $T$ - $S$  diagrams are particularly convenient and useful in the case of reversible cycles.



**Fig.**

Although the actual form of  $T$ - $S$  diagram depends on the actual reversible process in progress, yet in general (i) the isothermal process is represented by a horizontal line parallel to entropy axis (ii) the adiabatic process is represented by a vertical line parallel to temperature axis, on these diagrams.

These  $T$ - $S$  diagrams are also called tephigrams (particularly in meteorology)

i)  $T$ - $S$  diagram for a carnot cycle. The isothermal expansion along  $AB$  in the carnot cycle, is represented by a horizontal line  $A'B'$  on  $T$ - $S$  diagram. Since heat  $Q_1$  is absorbed at temperature  $T_1$  from the source, the gain in entropy along  $A'B' = \frac{Q_1}{T_1}$

The adiabatic expansion  $BC$  of the Carnot cycle is represented by  $B'C'$ , a vertical line, with no change in entropy, however, we have a fall in temperature from  $T_1$  to  $T_2$ .

The isothermal compression  $CD$  along which heat  $Q_2$  is rejected to the sink at  $T_2$  is represented by  $C'D'$ . The loss in entropy is  $\frac{Q_2}{T_2}$ . Finally, adiabatic compression  $DA$  of the Carnot cycle is represented by  $D'A$  on the  $T$ - $S$  diagram with no change in entropy. But we have a rise in temperature from  $T_2$  to  $T_1$ .

It will thus be seen that the curvilinear quadrilateral Carnot cycle on the indicator diagram becomes a rectangle on the tephigram. Further, the area of  $ABCD$  gives work done during a cycle  $AB'C'D$  on  $T$ - $S$  diagram gives the quantity of heat converted into work during the cycle and is therefore a *heat-diagram*.

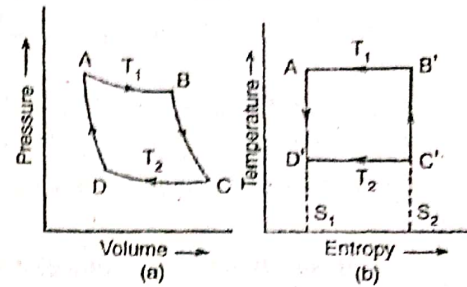


Fig.

$$\text{Area of } A'B'C'D' = AD' \times D'C' = (T_1 - T_2) (S_2 - S_1) = (T_1 - T_2) \left( \frac{Q_1}{T_1} - \frac{Q_2}{T_2} \right) = (Q_1 - Q_2)$$

.....(1)

$\therefore$  Change of entropy along  $AB' = D'C' = S_2 - S_1$ , as shown in Fig.

But change in entropy  $AB' = \frac{Q_1}{T_1}$  and change in entropy along  $(D'C') = \frac{Q_2}{T_2}$

$$\text{or } \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2} = S_2 - S_1$$

Relation (i) represents the heat energy converted into work.

Hence efficiency of engine

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\text{Heat energy converted into work}}{\text{Total heat absorbed}}$$

Which is the same as obtained by usual treatment of a Carnot cycle.

We may note that  $Q_2$  is the unavailable energy for work and

$$Q_2 = \frac{Q_1}{T_1} \times T_2 = \text{Gain in entropy} \times \text{temperature}$$

Thus, for a given temperature of the sink, the unavailable energy is proportional to the gain in entropy.

**Uses of T-S diagram or importance of T-S diagram :**

1. They are used in meteorology.
2. For calculating the work value of the fuel.
3. For finding out the defects in the working of the engine.
4. These are convenient and useful in the case of reversible cycles.



**Q. 5. Define entropy ? What is physical concept of entropy ? Write a note on entropy change in reversible and irreversible processes ?**

**Ans : Definition of entropy :** Clausius symbolised  $\frac{\delta Q}{T}$  as  $S$  and called it as entropy. Its change 'ds' is defined by the ratio of the heat change and the temperature at which the heat change occurs i.e.,

$$dS = \frac{\delta Q_{rev}}{T}$$

where  $\delta Q_{rev}$  is the heat absorbed reversibly by an infinitesimal portion of the system at temperature  $T$ .

If the heat change takes place at different temperatures then

$$dS = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} + \frac{\delta Q_3}{T_3} + \dots = \sum \frac{\delta Q_{rev}}{T}$$

Eqn. (2) can be written as  $\int dS = \int \frac{\delta Q_{rev}}{T}$  or  $S = \int \frac{\delta Q_{rev}}{T}$

From the above equation it follows that "the entropy difference between two states of a given system is equal to the summation of all the  $\frac{Q_{rev}}{T}$  terms of all the steps necessary to bring about a reversible transformation between these two states, where  $Q_{rev}$  stands for the heat absorbed reversibly and  $T$  the corresponding temperature.

**Physical significance of entropy :** We will now discuss some aspects which will provide a definite physical significance to entropy.

**1. Entropy and unavailable energy :** The internal energy of any substance is composed of various contributions. A part might be the kinetic energy of molecules, another part might be the vibrational energy of the molecules, another part might be due to intermolecular attraction and the remaining parts might be distributed in various other ways.

Second law teaches us that all these various contributions of energy are not equally convertible into useful work. Without caring to consider which part of these different forms of internal energy is useful, the second law tells us that a portion of this energy is always unavailable and entropy is a measure of this unavailable energy. In fact we can regard the entropy as the unavailable energy per unit temperature, i.e., entropy multiplied by the temperature ( $^{\circ}\text{K}$ ) gives the total quantity of energy which is unavailable for useful work.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

$$\text{or Unavailable energy} = \text{Entropy} \times \text{Temperature}$$

**2. Entropy as an Order-disorder phenomenon :** Whenever a spontaneous process (such as the flow of heat in a metal bar from the hot to the cold end, diffusion of one gas into another, the dissolution of a solid by a solvent etc) proceeds, it is accompanied by an increase in the "disorder" or "randomness" of the molecules constituting the system. In all such process there also occurs an increase of entropy. Hence entropy can be regarded as "a measure of disorder or random arrangement of the molecules in a system."

We will illustrate the concept of "disorder" or "randomness" of a system by reference to Fig. When a gas is at low pressure, the molecules are free to move freely in all possible directions.

When the pressure of the gas is increased, the same number of molecules are forced to occupy a smaller volume so that the chances of finding a molecule within a specified region are greater than before. Thus, the degree of disorder has decreased and there occurs a greater "order" in the system.

The molecules now are very much closer together than in the gaseous state. They are in an even more highly "ordered" state than in the gas at high pressure.

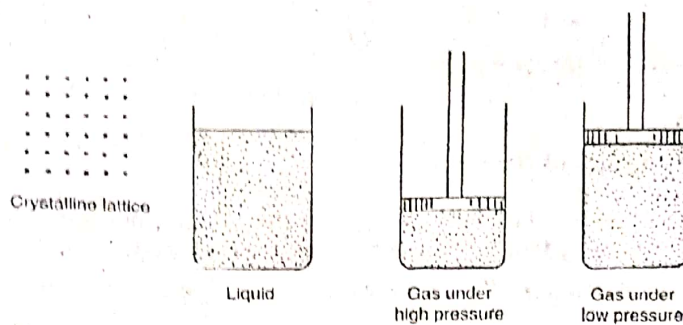


Fig.

If the temperature is further lowered to the freezing point, the liquid passes into the solid state. The molecules, atoms or ions in the solid state are no longer free to move away from each other. The only freedom that they possess is that of vibration or rotation which also become zero at  $0^\circ\text{K}$ , i.e., an "absolute order" prevails. The degree of disorder is now considered to be zero.

The gradual decrease in the degree of "freedom" or "disorder" as a substance passes from the gaseous to the solid state is identifiable with change of entropy which is very high for a gas and low for a solid. At  $0^\circ\text{C}$ , the entropy of a solid is considered to be zero.

**Units of entropy :** The dimensions of entropy are Energy  $\times$  Temperature<sup>-1</sup>. The entropy is expressed as calories per degree which is sometimes referred to as the "entropy units" (e.u). Since entropy depends on the quantity of the substance involved, the same must also be stated clearly. Thus, one can say that entropy units are "calories per degree per mole" or "calories per gram" etc.

**Change in Entropy in a reversible process (Carnot's cycle) :** Consider a reversible Carnot's cycle  $ABCD$  shown in Fig. From  $A$  to  $B$  the working substance absorbs a quantity of heat  $Q_1$  at  $T_1$  during the isothermal expansion.

$$\text{Hence, increase in entropy} = \frac{Q_1}{T_1}$$

During the isothermal compression  $CD$ , the working substance rejects a quantity of heat  $Q_2$  at  $T_2$ .

$$\text{Hence, decrease in Entropy} = \frac{Q_2}{T_2}$$

During the adiabatic compression  $DA$  (which finally completes the cycle) again there is no change in entropy,

$\therefore$  Net change in entropy of the working

$$\text{Substance in the cycle } ABCDA = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

But by the definition of absolute scale of temperature,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \therefore \frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

Hence, the total change in entropy of the working substance in a Carnot's reversible cycle is zero.

**Change in Entropy in an irreversible process :** During an irreversible process like conduction or radiation, heat is lost by a body at higher temperature  $T_1$  and is gained by a body at lower temperature  $T_2$  i.e.  $T_1 > T_2$ .

Let  $Q$  be the quantity of heat given out by the hot body at temperature  $T_1$  and the quantity of heat gained by the cold body at temperature  $T_2$  be  $Q$ . Considering the hot and cold bodies as one system.



Decrease in entropy of the hot body =  $\frac{Q}{T_1}$

and increase in entropy of the cold body =  $\frac{Q}{T_2}$

$\therefore$  Total increase in entropy of the system =  $\frac{Q}{T_1} - \frac{Q}{T_2}$

It is a +ve quantity as  $T_2 < T_1$ . Thus the entropy of the system increases in all irreversible process.

### SHORT ANSWER QUESTIONS

**Q. 1. Difference between Isothermal and Adiabatic processes.**

**Ans :** a) Isothermal change is a process in which a change in pressure and volume of a substance takes place keeping the temperature constant. Adiabatic change is a process in which a change in pressure and volume of a substance takes place keeping it thermally insulated from the surroundings.

b) During isothermal process, the gas is enclosed in a metallic cylinder while in an adiabatic process the gas is in a non-conducting cylinder.

c) Isothermal change is a slow process while adiabatic change is a quick process.

d) During an isothermal change, the temperature of the gas remains constant, while in an adiabatic change the temperature of the gas does not remain constant.

e) An isothermal change is represented by Boyle's law given by the equation  $PV = \text{constant}$ .

An adiabatic change is represented by Poissons's law given by the equation  $PV^\gamma = \text{constant}$ .

f) The work done in isothermal process is  $W = 2.3026 RT \log \frac{V_2}{V_1}$ . The work done in adiabatic process

is  $W = \frac{R}{\gamma - 1} (T_2 - T_1)$

g) There is an exchange of heat from system to surroundings and surroundings to system in isothermal process. But in adiabatic there is no such exchange of heat.

h) Melting of ice at its melting point is isothermal. Burst of a motor tyre is adiabatic.

**Q. 2. Define Reversible and irreversible processes ? Give examples.**

**Ans : Reversible process :** A reversible process is one which can be traced in the opposite direction so that the working substance passes through exactly the same stages in the opposite direction as in the direct process. For example, in a certain path where heat is absorbed in the direct process, it is given out in the reverse process and vice versa. Similarly in a certain path, where work is done on the working substance in the direct process an equal amount of work is done by the working substance in the reverse process and vice versa.

**Irreversible Process :** An irreversible process is one which cannot be retraced in the opposite direction by reversing the controlling factors.

The Examples of Reversible Process :

1. Isothermal and Adiabatic expansion and compression of a perfect gas when performed slowly.
2. Conversion of solid into liquid or viceversa at the same temperature.
3. Conversion of liquid into vapour or viceversa at the same temperature.

The Examples of irreversible Process :

1. Work done in overcoming friction.
2. Joule Thomson effect is irreversible, since on reversing the direction of flow of the gas there is no change in the cooling or heating effect.
3. Heat produced in a conductor when electric current flows through it.
4. Conduction of heat through a metallic bar.

**Q. 3. Define second law of thermodynamics ? Write the applications for it ?**

**Ans : Clausius statement :** Heat cannot by itself, without performance of work by an external agency, pass from a body at a lower temperature to one at higher temperature.

**Kelvin's statement :** It is impossible to derive a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.

**Explanation :** When the Carnot engine works in reverse order it absorbs heat from the sink (body of lower temperature) and rejects heat to the source (body of higher temperature) and in this case work is done on the engine. This explains the Clausius statement.

When the Carnot engine works between the temperatures  $T_1$ ,  $T_2$  its efficiency is ( ). In this process heat  $Q_1$  is absorbed from the source at  $T_1$  and rejects heat  $Q_2$  to the sink at  $T_2$ . In this process the heat energy ( $Q_1 - Q_2$ ) is converted only mechanical energy. This can be continued until ( $T_1 - T_2$ ) and on further cooling the source the heat energy cannot be converted into mechanical energy. This explains kelvin's statement.

**Application of the second law of thermodynamics :**

**Clausius-Clapeyron Equation :** It relates the change in the boiling point or the freezing point of a substance with increase in pressure. We will derive here the expression.

Let  $EBA$  and  $GHIJ$  represent two isotherms for a substance at  $T$  and  $T - dT$  temperatures respectively, below its critical point. Then if the change of state involved be from vapour to liquid (or vice versa) we have the substance existing only in its vapour phase at  $B$  and  $H$  and only in its liquid phase at  $A$  and  $I$  whereas along  $BA$  and  $HI$  the change of state is actually in progress and the substance therefore exists in both phases, vapour and liquid. Clearly  $T$  is the boiling point of the liquid at pressure  $P - dP$  corresponding to point  $I$ . Similarly, if the change of state were from liquid to solid (or vice versa) we have substance only in its liquid phase at  $B$  and  $H$  and only in its solid phase at  $A$  and  $I$ . Along  $AB$  and  $IH$  the change of state is in actual progress.  $T$  and  $T - dT$  are then melting points of the solid at pressure  $P$  (point  $A$ ) and at pressure ( $P - dP$ ) at point  $I$ ) respectively.

Let  $AD$  and  $BC$  be two adiabatic joining isotherms  $AB$  and  $DC$ . Then work done in one cycle  $ABCD$  is  $dW$  and is related to heat quantities and temperatures by

$$\frac{dW}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1} = T - \frac{(T - dT)}{T} = \frac{dT}{T}$$

If  $dT$  be small, Carnot cycle is a parallelogram of area  $(V_2 - V_1) dP$ . If the mass of the substance is unity then the quantity of heat absorbed during the change of state is the latent heat  $L$ , at temperature  $T$ . Then in units of work

$$\frac{(V_2 - V_1) dP}{L} = \frac{dT}{T} \quad [\because Q_1 = L] \quad (or) \quad \left( \frac{dP}{dT} \right)_{dt=0} = \frac{1}{T(V_2 - V_1)}$$

This is called the first Latent heat equation or Clausius - Clapeyron equation.  $\frac{dP}{dT}$  is the rate at which saturated vapour pressure of a liquid increases with the temperature.

Clearly, the sign of  $\frac{dP}{dT}$  will depend on the sign of  $(V_2 - V_1)$ . It is always positive for liquid to vapour state changes. Therefore, boiling point of a liquid must rise with increase in pressure (and vice versa).

In the case of liquid solid phase changes the difference in specific volume may not always hence for solids which expand on melting, the melting point rises with increase in pressure whereas those which contract on melting the melting point lowers with increase in pressure.

**Special case :** When  $V_2 = V_1$ . In this case change in specific volume is zero then either  $L = 0$ , or

$$\frac{dP}{dT}$$



i)  $L = 0$  at a temperature close to critical point and a liquid passes into vapour state with little or no absorption of heat.

ii)  $\frac{dP}{dT} \rightarrow \infty$  or very large at fusion for most of the solids.

The latent heat has two components  $L = L_i + L_e$  where  $L_i$  is internal energy of the liquid and  $L_e$  is heat required in doing external work  $= P(V_g - V_l)$

We can find  $L_i = L - L_e = (V_g - V_l) \frac{dP}{dT} = P(V_g - V_l)$

$$L_i = T(V_g - V_l) \left( \frac{dP}{dT} - \frac{P}{T} \right) = T^2(V_g - V_l) \frac{d}{dT} \left( \frac{P}{T} \right)$$

**Q. 4. State and explain first law of thermodynamics ?**

**Ans :** The first law of thermodynamics is simply the principle of conservation of energy applied to a thermodynamic system. It can be stated as whenever other forms of energy are converted into heat or vice versa there is a fixed ratio between the quantities of energy and of heat thus converted. The first law of thermodynamics asserts that 1. Heat is a form of energy and 2. Energy is conserved in a thermodynamic system. The first law of thermodynamics can be mathematically stated in the form  $dQ = du + dw$ .

Where  $dQ$  is the quantity of heat absorbed by the system,  $du$  the increase in its internal energy and  $dw$  the amount of work done by it.

**Significance of First law :** This law establishes an exact relation between heat and work. It tells us that a certain quantity of heat will produce of definite amount of work and vice-versa. The first law of thermodynamics denies that work or energy can be produced from nothing. Work can not appear without disappearance of heat.

**Limitation of first law :** According to the first law of thermodynamics, there is an exact equivalence between various forms of energy. This law also tells us that if a process takes place, energy is converted into equivalent amount of work. But the first law does not give any information regarding the conditions and to what extent it is possible to convert one form of energy into another.

**Applications of first law to some particular cases :**

**The specific Heat :** We know that the internal energy of a system is a single valued function of thermodynamic variables  $P$ ,  $V$  and  $T$ . Any two of these may be treated as independent. Let  $U = f(V, T)$

$$\text{or, } dU = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV \quad \dots(i)$$

Now for a perfect gas, according to first law

$$\partial Q = dU + PdV$$

$$\text{or } \partial Q = \left( \frac{\partial U}{\partial T} \right)_V dT + \left( \frac{\partial U}{\partial V} \right)_T dV + PdV \text{ from } \dots(1)$$

$$\text{or } \frac{\partial Q}{\partial T} = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial V}{\partial T} \right) \left( \frac{\partial U}{\partial V} \right)_T + P \left( \frac{\partial V}{\partial T} \right)$$

$$\text{or } C_v + \frac{dV}{dT} \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \quad \dots(2)$$

If gas is heated at a constant pressure then

$$\left(\frac{\partial Q}{\partial T}\right)_p = C_v + \left(\frac{dV}{dT}\right)_p \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

$$\text{or } Cp = C_v + \left(\frac{dV}{dT}\right)_p \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \quad \dots\dots(3)$$

But we know that at constant temperature there is no change in internal energy i.e.,  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  and for a perfect gas  $PV = RT$  or  $PdV = RdT$

$$\text{i.e., } P \left(\frac{dV}{dT}\right)_p = R$$

**Q. 5. Explain thermo dynamic scale of Temperature ? Explain How it is perfect to absolute scale ?**

**Ans :** The efficiency of a Carnot's engine depends only on the temperatures of the source and the sink. So the property, that the work done by the Carnot's engine depends only on the difference of temperatures of Source  $T_1$  and Sink  $T_2$ , can be utilised to measure  $T_1 - T_2$ . The thermometers, other than this, depended on some property of thermometric substance. So there was no ideal thermometric scale, the absolute scale. When the temperature measured on then did not agree with one another. Lord Kelvin propounded the idea of absolute scale with following sequence of arguments.

Let one Carnot engine be working between  $\theta_1$  and  $\theta_2$  temperatures measured on any arbitrary scale then

$$f = f(\theta_1, \theta_2) \text{ where } f \text{ is some function of } \theta_1 \text{ and } \theta_2$$

$$\text{But we know } \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = f(\theta_1, \theta_2)$$

$$\therefore \frac{Q_1}{Q_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2)$$

where  $F$  is some other function.

Let another Carnot engine be working between  $\theta_2$  and  $\theta_3$  temperature limits, then

$$\frac{Q_2}{Q_3} = F(\theta_2, \theta_3)$$

Let another Carnot engine be works between  $\theta_1$  and  $\theta_3$ . Such that  $\frac{Q_1}{Q_3} = F(\theta_1, \theta_3)$

$$\text{From (i) and (ii) } \left(\frac{Q_1}{Q_2}\right) \left(\frac{Q_2}{Q_3}\right) = F(\theta_1, \theta_2) F(\theta_2, \theta_3) \text{ or, } \frac{Q_1}{Q_3} = F(\theta_1, \theta_2) F(\theta_2, \theta_3)$$

$$\text{or, } F(\theta_1, \theta_3) = F(\theta_1, \theta_2) F(\theta_2, \theta_3)$$

In order that this functional equations be satisfied  $F(\lambda)$  should be of the form  $\frac{\phi(\theta_1)}{\phi(\theta_2)}$  i.e.,

$$\frac{Q_1}{Q_2} = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$



$\phi(\theta)$  is thus a quantity which increases monotonously with  $\theta$  and hence can be used to measure the temperature. Kelving chose the linear function  $\phi(\theta)$  to represent directly the temperature of the working substance of the engine. Denoting  $\phi(\theta)$  by  $\lambda$  we have

$$\frac{Q_1}{Q_2} = \frac{\lambda_1}{\lambda_2}$$

This relation is the new scale of temperature and is called the absolute or the work of the thermodynamical scale of temperature. Thus the thermodynamic temperature scale is defined so that (1) the ratio of the thermodynamic temperature of the two reservoirs is equal to the ratio of the amounts of heats exchanged among these reservoirs by Carnot engines working between their temperatures (2) the ratio of the thermodynamic temperatures is independent of the nature of the working substance, and depends only on the property that is common to all substances.

Temperatures measured on this scale are in Kelvin. The efficiency here, is again

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\lambda_1 - \lambda_2}{\lambda_1} = \frac{T_1 - T_2}{T_1}$$

$T_2 = 0$ ,  $Q_2 = 0$  and the efficiency of the engine is unity. Thus the zero of the thermodynamic scale is that temperature of the sink at which no heat is rejected and all the heat taken from the source is converted into useful work. A temperature lower than absolute zero is not possible as it would implies  $\eta > 1$ . According to Kelvin's statement  $Q_1 \neq W$  i.e.,  $Q_1 - Q_2 < Q_1$  or,  $Q_2 \neq 0$ , then lowest attainable temperature will be greater than absolute zero.

**Q. 6. Deduce the expression for the change of entropy when ICE changes into steam ?**

**Ans :** Here we shall find an expression for the change of entropy when  $m$  gm of ice at  $T_1^0$  K changes into steam at  $T_2^0$  K. Let  $L_1$  and  $L_2$  be the latent heats of fusion and vapourisation respectively.

i) First of all  $m$  gm ice at  $T_1^0$  K changes into water at  $T_2^0$  K, i.e., there is no change in temperature. The change in entropy is given by

$$\Delta S_1 = \frac{mL_1}{T_1} \quad \dots(1)$$

ii) Secondly  $m$  gm water at  $T_1^0$  K changes into water at  $T_2^0$  K. The change of entropy is given by

$$\Delta S_2 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{mc dT}{T} = mc \log_e \left( \frac{T_2}{T_1} \right) \quad \dots(2)$$

where  $c$  is the specific heat capacity of water

iii) Finally  $m$  gm of water at  $T_2^0$  K changes into steam at  $T_2^0$  K. The change in entropy is given by

$$\Delta S_3 = \frac{mL_2}{T_2} \quad \dots(3)$$

The total change in entropy when ice is converted into steam

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 \quad \text{or} \quad \Delta S = \frac{mL_1}{T_1} + mc \log_e \left( \frac{T_2}{T_1} \right) + \frac{mL_2}{T_2}$$

$$\text{or } \Delta S = \frac{mL_1}{T_1} + 2.3026 mc \log_{10} \left( \frac{T_2}{T_1} \right) + \frac{mL_2}{T_2} \quad \dots(4)$$

**Q. 7. Deduce the expression for the change in entropy of the universe ?**

**Ans :** We will now show that the entropy of the universe remains constant in a reversible process but increases in an irreversible one. If a system undergoes a physical or a chemical process, there is a change in the entropy of the system and also in its local surroundings. This total change in the entropy of the system and its surroundings is called the entropy change of the universe brought about by the process.

Let us first consider the entropy change of the universe due to any reversible process.

**a) Entropy change of the Universe in Reversible process :** Let us consider a Carnot's cycle consider the first stage represented by  $AB$ . In this process the working substance absorbs heat  $Q_1$  from the reservoir at temperature  $T_1$ . This results in an increase in the entropy of the working substance given by

$$(S_B - S_A)_{\text{system}} = \frac{Q_1}{T_1} \quad \dots(1)$$

The surroundings lose the same amount of heat  $Q_1$  at the same temperature. The result is that there will be a change in the entropy of the surroundings as given by

$$(S_B - S_A)_{\text{sur}} = -\frac{Q_1}{T_1} \quad \dots(2)$$

therefore, the total change in the entropy of the universe due to an isothermal process is given by

$$\begin{aligned} (S_B - S_A)_{\text{rev}} &= (S_B - S_A)_{\text{system}} + (S_B - S_A)_{\text{sur}} \\ &= \frac{Q_1}{T_1} - \frac{Q_1}{T_1} = 0 \quad (\text{from equations (1) and (2)}) \end{aligned}$$

Hence, the change of the entropy of the universe during a reversible isothermal process is zero.

Now consider a reversible adiabatic curve  $BC$ . In this process the working substance does not transfer or take the heat from the surroundings, i.e.,  $Q = 0$ . Therefore, the change in entropy along reversible adiabatic  $BC$  is given by  $(S_C - S_B)_{\text{system}} = 0$  [ $Q = 0$ ]  $\dots(3)$

Similarly the surroundings does not undergo any heat change. It, therefore leads to

$$(S_C - S_B)_{\text{sur}} = 0 \quad \dots(4)$$

Therefore, the total change in entropy of the universe during reversible adiabatic process is

$$\begin{aligned} (S_C - S_B)_{\text{rev}} &= (S_C - S_B)_{\text{system}} + (S_C - S_B)_{\text{sur}} \\ &= 0 \quad (\text{from equations (3) and (4)}) \end{aligned}$$

It means that the entropy of the universe during a reversible adiabatic process is also zero. These adiabatics (like adiabatic  $BC$ ) of constant entropy are known as "isentropics".

Now consider the complete Carnot's cycle. The total change in the entropy over the Carnot's cycle

$$ABCD \text{ is given by } \left( \frac{Q_1}{T_1} + \frac{Q_2}{T_2} \right) \text{ or zero.}$$

Similarly the entropy change of the surroundings is also zero. Therefore, we conclude that the entropy of the Carnot's cycle in a reversible process remains unchanged.

$$\int dS = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$$

The integral sign denotes the summation over the complete cycle. Hence, the net increase in entropy in a Carnot's cycle is zero.

**b) Entropy change of the universe in an irreversible process :** In a irreversible process there is an increase in the entropy of the universe. This can be shown by assuming an irreversible conduction of heat  $Q$  from a body  $A$  at higher temperature  $T_1$  to another body at lower temperature  $T_2$ . Therefore, the change in the entropy of this irreversible process is given as



$$(\Delta S)_{irr} = \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} = dQ \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \quad \dots(1)$$

where  $\frac{\delta Q}{T_1}$  represents the decrease in entropy of body and  $\frac{\delta Q}{T_2}$  the entropy gained by B. At conduction of heat always takes place from a higher to lower temperature, it, therefore follows that  $T_1 > T_2$

$$(or) \frac{1}{T_2} > \frac{1}{T_1}; (or) \frac{\delta Q}{T_2} > \frac{\delta Q}{T_1}; (or) \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} > 0$$

Applying this condition to equation (1) we get  $(\Delta S)_{irr} > 0$

This condition implies that the entropy of the universe increases in an irreversible process like conduction, radiation etc.

**Principle of increase in Entropy :** In general, we can write entropy change for any reversible process

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0 \quad \dots(2)$$

and for any irreversible process,

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \dots > 0 \quad \dots(3)$$

on combining equations (2) and (3) we get

$$\Delta S_{irr} \geq 0 \quad \dots(4)$$

where the equality sign refers to a reversible process and the inequality sign to a irreversible process. But most of the natural process are irreversible in nature. This led to the principle of increase of entropy as :

"The energy of the universe remains constant and the entropy of the universe tends towards a maximum."

**Q. 8 Give relation between Thermodynamics and perfect gas scale ?**

**Ans :** The efficiency  $\eta$  of a reversible engine on the thermodynamic scale is given by

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

If  $T_2 = 0$  and  $Q_2 = 0$ , then the efficiency  $\eta = 1$ . Now  $T_2$  cannot be less than zero i.e., negative, because if it were so, the efficiency would be greater than 1, which is impossible.

Thus the zero on the thermodynamic scale is that temperature where the efficiency of a reversible engine becomes unity and further all the heat absorbed by the engine is converted to work.

On the gas scale the efficiency  $\eta$  is given by,

$$\eta = 1 - \frac{T_2}{T_1}$$

The value of  $\eta$  will again be unity only when  $T_2 = 0^\circ A$ . Now  $T_2$  cannot be less than  $0^\circ A$  i.e., negative, because if it were so, the efficiency would be greater than 1, which is impossible.

Hence zero of the perfect gas scale and that of the thermodynamic scale is the same.

As the efficiencies in both the cases have the same values.

$$\frac{T_2}{T_1} = \frac{T_1}{T_2}$$

If  $T_1$  and  $T_2$  represent the temperature of the boiling points of water and melting point of ice at normal pressure, then

$$T_1 - T_2 = 100$$

For the same fixed points on the thermodynamics scale,  $T_1 - T_2 = 100$

On the thermodynamic scale,  $\eta = \frac{T_1 - T_2}{T_1} = \frac{100}{T_1}$

and on the perfect gas scale,  $\eta = \frac{T_1 - T_2}{T_1} = \frac{100}{T_1}$

Since the efficiency is the same.  $\frac{100}{T_1} = \frac{100}{T_1}$  (or)  $T_1 = T_2$

This means that the boiling point of water or the melting point of ice (at normal pressure) are identical on both the scales.

In a similar manner it can be shown that any other temperature will have the same value on both the scales i.e., the two scales are identical.

**Q. 9. Explain about absolute scale of temperature (or) kelvin scale of temperature ?**

**Ans :** An absolute scale of temperature is one which independent of the properties of any particular substance. The various thermometers used for the measurement of temperature are based on the variation of some property of a material with heat (eg : Expansion of a solid, liquid or gas, change in resistance of platinum, development of thermo e.m.f. etc).

From Carnot's theorem it is clear the efficiency of a reversible engine depends only on the two temperatures (of the source and sink) between which it work, and is independent of the working substance. Taking this concept, Lord Kelvin defined a temperature scale which does not depend upon the properties of the working substance. This is known as the Kelvin's absolute thermodynamic scale of temperature.

**SOLVED PROBLEMS**

**Q. 1. A gram mole of air expands at constant temperature so that its volume changes from 2 litres to 10 litres. Find the work done by the gas. Initial pressure is 5 atmospheres.**

(Assume 1 atmosphere =  $10^5 \text{ N-m}^{-2}$ )

**Sol :** Work done by the gas,

$$\begin{aligned} W &= RT \log \frac{V_2}{V_1} = 2.303 PV \log_{10} \frac{V_2}{V_1} \quad (\because PV = RT) \\ &= 2.303 \times 5 \times 10^5 \times 2 \times 10^{-3} \log_{10} \left( \frac{10}{2} \right) = 2.303 \times 5 \times 10^5 \times 2 \times 10^{-3} \times \log_{10} (5) \\ &= 2.303 \times 5 \times 10^5 \times 2 \times 10^{-3} \times 0.6990 = 2.303 \times 10^6 \times 10^{-3} \times 0.6990 \\ &= 2.303 \times 0.6990 \times 10^3 \text{ Joules} = 1.61 \times 10^3 \text{ Joules} \end{aligned}$$

**Q. 2. If the temperature of the sink is  $27^\circ\text{C}$  and of the source is  $127^\circ\text{C}$ , calculate the efficiency of the Carnot engine.**

**Sol :**  $T_1 = 273 + 127 = 400 \text{ K}$ ,  $T_2 = 273 + 27 = 300 \text{ K}$

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{400 - 300}{400} = \frac{1}{4} = 0.25 = 25\%$$

**Q. 3. The temperatures of source and sink in a Carnot engine is  $800\text{K}$  and  $300 \text{ K}$ . Calculate the mechanical work done during a cycle if heat absorbed from the source is  $100 \text{ Calories}$ .**

**Sol :**  $T_1 = 800\text{K}$ ;  $Q_1 = 100 \text{ Calories}$ ,  $T_2 = 300 \text{ K}$ ;

Work done by the engine =  $Q_1 - Q_2 = ?$

$$\begin{aligned} \text{Since } \frac{Q_1 - Q_2}{Q_1} &= \frac{T_1 - T_2}{T_1} \quad Q_1 - Q_2 = Q_1 \frac{T_1 - T_2}{T_1} = 100 \times \frac{800 - 300}{800} \\ &= \frac{100 \times 500}{800} = 62.5 \text{ cal} = 62.5 \times 4.2 = 26.5 \text{ Joules} \end{aligned}$$



- Q. 4.** An ideal heat engine operates in a Carnot cycle between 227 and 127°C. It absorbs  $6.0 \times 10^4$  Calories at the higher temperature. How much work per cycle this engine can perform?

**Sol :**  $T_1 = 273 + 227 = 500 \text{ K}$ ,  $Q_1 = 6.0 \times 10^4 \text{ cal}$

$T_2 = 273 + 127 = 400 \text{ K}$

Workdone per cycle =  $W = Q_1 - Q_2 = ?$

$$\odot \frac{Q_1 - Q_2}{Q_1} = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = \frac{W}{6.0 \times 10^4} = \frac{500 - 400}{500} = \frac{1}{5}$$

$$W = \frac{1}{5} \times 6.0 \times 10^4 = 1.2 \times 10^4 \text{ calories} = 1.2 \times 18 \times 10^4 = 5 \times 10^4 \text{ Joules}$$

- Q. 5.** In a mechanical refrigerator the low temperature coils are at a temperature of -13°C and the compressed gas in the condenser has a temperature of 27°C. Find the theoretical coefficient of performance?

**Sol :**  $T_1 = 273 + 27 = 300 \text{ K}$ ,  $T_2 = 273 - 13 = 260 \text{ K}$ ;  $k = ?$

$$k = \frac{T_2}{T_1 - T_2} = \frac{260}{40} = 6.5$$

- Q. 6.** How much work must be done to transfer 1.0 joule of heat from the reservoir at 7°C to one at 27°C by means of a refrigerator using a Carnot cycle.

**Sol :**  $Q_2 = 1.0 \text{ Joule}$ ,  $T_1 = 273 + 27 = 300 \text{ K}$ ;  $W = ?$

$$\text{Since } \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2} \quad \frac{1.0}{W} = \frac{280}{300 - 280} = \frac{280}{20} = \frac{14}{1}$$

$$\therefore W = \frac{1.0}{14} = 0.071 \text{ Joule}$$

- Q. 7.** How is the efficiency of a reversible heat engine related to the co-efficient of performance of a reversible refrigerator obtained by running the engine backward?

**Sol :** The efficiency of a Carnot engine working between the temperature  $T_1$  and  $T_2$  of source and sink is

$$\eta = \frac{T_1 - T_2}{T_1} \quad \dots(1)$$

Coefficient of performance  $k$  is given by  $k = \frac{Q_2}{W} = \frac{T_2}{T_1 - T_2} \quad \dots(2)$

$$(1) \times (2) \quad \eta \times k = \frac{T_2}{T_1 - T_2}$$

- Q. 8.** Find the difference in entropy between 1 gram of water and 1 gram of steam at 100°C and at one atmospheric pressure.

(Latent heat of vapourisation of water = 540 cal/gm)

**Sol :** In this case to convert 1gm of water at 100°C to steam at 100°C under one atmospheric pressure, the latent heat  $Q = 540$  calories is absorbed. In this process the

Temperature = 100°C = 100 + 273 = 373 K is constant.

$$\text{Increase in entropy} = \frac{Q}{T} = \frac{540}{373} = 1.448 \text{ cal/K}$$

**Q. 9.** Calculate the change of entropy when 1 gm of ice at  $0^\circ\text{C}$  changes to 1 gm of steam at  $100^\circ\text{C}$ .

**Sol :** (Assume the specific heat of water = 1, latent heat of fusion of ice  $L_f = 80$  cal/gm and latent heat of vapourisation of water  $L_v = 540$  cal/gm)

$$\begin{aligned} S_{\text{steam}} - S_{\text{ice}} &= \frac{L_f}{T_1} + 2.303 \log_{10} \frac{T_2}{T_1} + \frac{L_v}{T_2} \\ &= \frac{80}{273} + 2.303 \log_{10} \frac{373}{273} + \frac{540}{373} \\ &= 0.293 + 0.312 + 1.448 \\ &= 2.052 \text{ cal/k} \end{aligned}$$

**Q. 10.** Find the change in entropy when 1 gm of steam at  $100^\circ\text{C}$  is condensed into water at  $0^\circ\text{C}$ .

**Sol :** In this case the entropy decreases. Decrease of entropy of the system

$$\Delta_s = \frac{L_v}{T_2} + \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta_s = \frac{L_v}{T_2} + \log \frac{T_2}{T_1}$$

$$= \frac{L_v}{T_2} + 2.303 \log_{10} \frac{T_2}{T_1}$$

$$= \frac{540}{373} + 2.303 \log_{10} \frac{373}{273}$$

$$\Delta_s = 1.448 + 0.312 = 1.760 \text{ cal/k}$$

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# UNIT - III

## THERMODYNAMICS POTENTIALS AND MAXWELL'S EQUATIONS

### LONG ANSWER QUESTIONS

**Q. 1.** Explain the concept of thermodynamic potentials? Deduce the Maxwell's equations from thermodynamic potentials? Give their significance.

**Ans :** Any thermodynamical system can be represented in terms of pressure, volume, temperature and entropy. These are named as thermodynamical variables. We know the first and second laws of thermodynamics can be written as follows.

$$dQ = dU + dW \qquad dQ = dU + PdV \qquad dQ = TdS$$

To know the complete idea of the system, we require other relations also. For that purpose, we have to use energy terms or functions of thermodynamical variables which are known as "thermodynamic potentials". So thermodynamic functions or potentials are energy functions which are developed by combining the thermodynamical variables. The thermodynamical potentials are 1. Internal energy ( $U$ ), 2. Helmholtz function ( $F$ ), 3. Enthalpy or total heat function ( $H$ ), 4. Gibbs function ( $G$ ).

**Maxwell's equations from Thermodynamic Potentials :**

**1. Internal energy ( $U$ ) :** The internal energy of the system is the energy due to motion of molecules and due to mutual attraction of molecules, we know

$$\begin{aligned} dQ &= dU + dW \\ dU &= dQ - dW \\ dU &= dQ - PdV \end{aligned} \qquad \dots(1)$$

$$\text{But } dS = \frac{dQ}{T} \qquad \therefore dQ = TdS \qquad \therefore dU = TdS - PdV$$

$$\text{From this } \left[ \frac{\partial U}{\partial S} \right]_V = T ; \left[ \frac{\partial U}{\partial V} \right]_S = -P$$

Since  $dU$  is a perfect differential, hence we can write

$$\frac{\partial}{\partial V} \left[ \frac{\partial U}{\partial S} \right]_V = \frac{\partial}{\partial S} \left[ \frac{\partial U}{\partial V} \right]_S \qquad \dots(1)$$

$$\therefore \left[ \frac{\partial T}{\partial V} \right]_S = - \left[ \frac{\partial P}{\partial S} \right]_V \qquad \frac{\partial}{\partial V} \left[ \frac{\partial U}{\partial S} \right]_V = \frac{\partial}{\partial S} \left[ \frac{\partial U}{\partial V} \right]_S$$

$$\therefore \left[ \frac{\partial T}{\partial V} \right]_S = - \left[ \frac{\partial P}{\partial S} \right]_V \qquad \dots(1)$$

This is Maxwell's first thermodynamic relation

**2. Helmholtz function ( $F$ ) :** We know  $dU = TdS - PdV$

If we consider a process in which temperature is constant then

$$\begin{aligned} TdS &= d(TS) \\ dU &= d(TS) - PdV \\ d(U - TS) &= -PdV \\ d(U - TS) &= -PdV \end{aligned}$$

Hence  $(U - TS)$  is represented by  $F$  named as Helmholtz free energy or Helmholtz function'

$$\therefore dF = -PdV$$

When the system changes from one equilibrium to another equilibrium, then  $F = (U - TS)$

$$dF = dU - TdS - SdT$$

But we know,  $dV = TdS - PdV$

$$dF = (TdS - PdV) - TdS - SdT \quad dF = -PdV - SdT$$

From this we can write

$$\left[ \frac{\partial F}{\partial V} \right]_T = -P \left[ \frac{\partial F}{\partial T} \right]_V = -S \quad \therefore \left[ \frac{\partial S}{\partial V} \right]_T = \left[ \frac{\partial P}{\partial T} \right]_V$$

Since  $dF$  is a perfect differential

$$\begin{aligned} \therefore \frac{\partial}{\partial V} \left[ \frac{\partial F}{\partial T} \right]_V &= \frac{\partial}{\partial T} \left[ \frac{\partial F}{\partial V} \right]_T & \therefore \frac{\partial}{\partial V} \left[ \frac{\partial F}{\partial T} \right]_V &= \frac{\partial}{\partial T} \left[ \frac{\partial F}{\partial V} \right]_T \\ \therefore \left[ \frac{\partial S}{\partial V} \right]_T &= - \left[ \frac{\partial P}{\partial T} \right]_V \end{aligned}$$

This is second thermodynamical relation.

**3. Enthalpy (H) (or) Total heat function :** It can be represented mathematically by  $H = U + PV$

Here  $H$  is the total heat content. This is heat function at constant pressure.

$$dH = dU + PdV + VdP$$

$$\text{But } dU = TdS - PdV$$

$$dH = [TdS - PdV] + PdV + VdP$$

$$dH = TdS + VdP$$

$$\text{From this we can write, } \left[ \frac{\partial H}{\partial S} \right]_P = T \left[ \frac{\partial H}{\partial P} \right]_S = V$$

Since  $dH$  is a perfect differential we can write

$$\frac{\partial}{\partial P} \left[ \frac{\partial H}{\partial S} \right]_P = \frac{\partial}{\partial S} \left[ \frac{\partial H}{\partial P} \right]_S$$

$$\therefore \left[ \frac{\partial T}{\partial P} \right]_S = \left[ \frac{\partial V}{\partial S} \right]_P$$

This is third thermodynamic relation.

**4. Gibbs function (G) :**

We know  $H = U + PV$

$$dH = dU + PdV + VdP$$

$$\text{But } dU = TdS - PdV$$

$$dH = (TdS - PdV) + PdV + VdP$$

$$dH = TdS + VdP$$

If we consider isothermal process then  $TdS = d(TS)$

If consider isobaric process where the pressure is constant then

$$dP = 0$$

$$dH = d(TS)$$

$$d(H - TS) = 0$$

$$H - TS = \text{constant}$$

This is represented by  $G$  named as Gibbs function.



$$G = H - TS$$

$$dG = dH - TdS - SdT$$

But we know  $dH = TdS + VdP$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

From this we can write

$$\therefore \left[ \frac{\partial G}{\partial T} \right]_P = - \left[ \frac{\partial G}{\partial P} \right]_T = V$$

Since  $dG$  is a perfect differential we can write,

$$\frac{\partial}{\partial T} \left[ \frac{\partial G}{\partial P} \right]_T = \frac{\partial}{\partial P} \left[ \frac{\partial G}{\partial T} \right]_P$$

$$\therefore \left[ \frac{\partial V}{\partial T} \right]_P = - \left[ \frac{\partial S}{\partial P} \right]_T$$

This is fourth thermodynamical relation.

**Significance of potentials :** These are very much useful in studying the equilibrium conditions of a system.

**Q. 2. Derive the Maxwell's thermodynamical relations from thermodynamical laws ?**

**Ans : Maxwells Equations from Thermodynamics Laws :** From the two laws of thermodynamics, Max-well deduced six fundamental thermodynamical relations. The state of a system can be defined by any pair of quantities viz., pressure (P) volume (V) temperature (T) and entropy (S). In order to solve any thermodynamical problem the most suitable pair is chosen and the quantities consulting the pair are independent variables. From the first law of thermodynamics.

$$dQ = dU + dW$$

or  $dQ = dU + PdV$

or  $dU = dQ - PdV$  ....(A)

From the second law of thermodynamics,

$$ds = \frac{dQ}{T} \text{ or } dQ = TdS$$
 ....(B)

Substituting equation (B) in (A) we get

$$dU = TdS - PdV$$
 .... (1)

Let us consider  $S$ ,  $U$  and  $V$  to be functions of two independent variables  $x$  and  $y$  (here  $x$  and  $y$  may be any two variables out of  $P$ ,  $V$ ,  $T$  and  $S$ ).

$$dS = \left( \frac{\partial S}{\partial x} \right)_y dx + \left( \frac{\partial S}{\partial y} \right)_x dy \quad dU = \left( \frac{\partial U}{\partial x} \right)_y dx + \left( \frac{\partial U}{\partial y} \right)_x dy$$

$$dV = \left( \frac{\partial V}{\partial x} \right)_y dx + \left( \frac{\partial V}{\partial y} \right)_x dy$$

On substituting these values in equation (1) we get

$$\left( \frac{\partial U}{\partial x} \right)_y dx + \left( \frac{\partial U}{\partial y} \right)_x dy = T \left[ \left( \frac{\partial S}{\partial x} \right)_y dx + \left( \frac{\partial S}{\partial y} \right)_x dy \right] - P \left[ \left( \frac{\partial V}{\partial x} \right)_y dx + \left( \frac{\partial V}{\partial y} \right)_x dy \right]$$

$$\left(\frac{\partial U}{\partial X}\right)_y dx + \left(\frac{\partial U}{\partial Y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial X}\right)_y - P\left(\frac{\partial V}{\partial X}\right)_y\right] dx + \left[\left(\frac{\partial S}{\partial Y}\right)_x - P\left(\frac{\partial V}{\partial Y}\right)_x\right] dy$$

On comparing the co-efficients of  $dx$  and  $dy$  in (1A) and (1B), we get

$$\left(\frac{\partial U}{\partial X}\right)_y = T\left(\frac{\partial S}{\partial X}\right)_y - P\left(\frac{\partial V}{\partial X}\right)_y \quad \left(\frac{\partial U}{\partial Y}\right)_x = T\left(\frac{\partial S}{\partial Y}\right)_x - P\left(\frac{\partial V}{\partial Y}\right)_x$$

Differentiating equation (2) with respect to  $y$  and equation (3) with respect to  $x$ , we get

$$\frac{\partial^2 U}{\partial Y \partial X} = \left(\frac{\partial T}{\partial Y}\right)_x \left(\frac{\partial S}{\partial X}\right)_y + T \frac{\partial^2 S}{\partial Y \partial X} - \left(\frac{\partial P}{\partial Y}\right)_x \left(\frac{\partial V}{\partial X}\right)_y - P \frac{\partial^2 V}{\partial Y \partial X}$$

$$\text{and } \frac{\partial^2 U}{\partial Y \partial X} = \left(\frac{\partial T}{\partial X}\right)_y \left(\frac{\partial S}{\partial Y}\right)_x + T \frac{\partial^2 S}{\partial X \partial Y} - \left(\frac{\partial P}{\partial X}\right)_y \left(\frac{\partial V}{\partial Y}\right)_x - P \frac{\partial^2 V}{\partial X \partial Y}$$

The change in internal energy brought about by changing  $V$  and  $T$ , whether  $V$  is changed by  $dT$  first and  $T$  by  $dV$  later or vice versa is the same. It means that  $dE$  is a perfect differential. Therefore,

$$\frac{\partial^2 U}{\partial Y \partial X} = \frac{\partial^2 U}{\partial X \partial Y} \left(\frac{\partial T}{\partial Y}\right)_x \left(\frac{\partial S}{\partial X}\right)_y + \frac{\partial^2 S}{\partial Y \partial X} - \left(\frac{\partial P}{\partial Y}\right)_x \left(\frac{\partial V}{\partial X}\right)_y - P \frac{\partial^2 V}{\partial Y \partial X}$$

$$= \left(\frac{\partial T}{\partial X}\right)_y \left(\frac{\partial S}{\partial Y}\right)_x + T \frac{\partial^2 S}{\partial X \partial Y} - \left(\frac{\partial P}{\partial X}\right)_y \left(\frac{\partial V}{\partial Y}\right)_x - P \frac{\partial^2 V}{\partial X \partial Y}$$

$$\therefore \frac{\partial^2 S}{\partial Y \partial X} = \frac{\partial^2 S}{\partial X \partial Y}; \frac{\partial^2 V}{\partial Y \partial X} = \frac{\partial^2 V}{\partial X \partial Y}$$

$$\therefore \left(\frac{\partial T}{\partial Y}\right)_x \left(\frac{\partial S}{\partial X}\right)_y - \left(\frac{\partial P}{\partial Y}\right)_x \left(\frac{\partial V}{\partial X}\right)_y = \left(\frac{\partial T}{\partial X}\right)_y \left(\frac{\partial S}{\partial Y}\right)_x - \left(\frac{\partial P}{\partial X}\right)_y \left(\frac{\partial V}{\partial Y}\right)_x$$

where  $x$  and  $y$  can be any two variables out of  $P, V, T$  and  $S$ .

#### Derivation of Relations :

**i) Relation I :** Taking  $T$  and  $V$  as independent variables

and  $x = T$  and  $y = V$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial V}{\partial y} = 1 \text{ and } \frac{\partial T}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

On substituting these values in equation (4), we get  $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\text{But } ds = \frac{dQ}{T} \quad \therefore \left(\frac{\partial Q}{\partial V}\right)_T = -T \left(\frac{\partial P}{\partial T}\right)_V$$

**ii) Relation II :** Taking  $T$  and  $P$  as independent variables and  $x = T, y = P$

$$\therefore \frac{\partial T}{\partial x} = 1, \frac{\partial P}{\partial y} = 1 \text{ and } \frac{\partial T}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$



On substituting these values in equation (4) we obtain

$$\left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x = \left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore dS = \frac{dQ}{T} \quad \therefore \left(\frac{\partial Q}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P$$

iii) **Relation III** : Taking  $S$  and  $V$  as independent variables and  $X = S, Y = V$

$$\therefore \frac{\partial S}{\partial x} = 1, \frac{\partial V}{\partial y} = 1 \text{ and } \frac{\partial S}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

On substituting these values in equation (4) we get

$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_V \quad \therefore dS = \frac{dQ}{T}$$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_S = -T \left(\frac{\partial P}{\partial Q}\right)_V$$

iv) **Relation IV** : Taking  $S$  and  $V$  as independent variables and  $x = S, y = P$

$$\therefore \frac{\partial S}{\partial x} = 1, \frac{\partial P}{\partial y} = 1 \text{ and } \frac{\partial S}{\partial y} = 0, \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (4) we get

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\text{or } \left(\frac{\partial T}{\partial P}\right)_S = T \left(\frac{\partial V}{\partial Q}\right) \left[ \therefore dS = \frac{dQ}{T} \right]$$

v) **Relation V** : Taking  $P$  and  $V$  as independent variables  $X = P$  and  $Y = V$

$$\frac{\partial P}{\partial x} = 1, \frac{\partial V}{\partial y} = 1, \frac{\partial P}{\partial y} = 0, \frac{\partial V}{\partial x} = 0$$

On substituting these values in equation (4) we get

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1$$

vi) **Relation VI** : Taking  $T$  and  $S$  as independent variables and  $x = T$  and  $y = S$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0, \frac{\partial S}{\partial x} = 0$$

Substituting these values in equation (4) we get

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1$$

These are the important thermodynamical relations, While solving a particular problem, the suitable equation is to be used.

Q. 1. Explain Joule-Kelvin effect? Deduce the expression for Joule-Kelvin coefficient for ideal and van der Waals gases?

Ans: When a purified gas is allowed to pass through a porous plug under constant pressure, the gas during its passage through the pores or fine holes becomes throttled. The gas thus suffers the volume expansion. On either sides of the plug the pressures  $P_1, P_2$  are applied. The entire arrangement is surrounded by a non conducting jacket and the process is adiabatic, i.e. no heat enters or leaves the system. In this process the total heat function  $H = U + PV$  remains constant. In this process in general there will be a change in temperature of the gas. This temperature change is referred to as the "Joule-Thomson" or the "Joule-Kelvin" effect.

**Explanation of Joule-Kelvin effect:** In the porous plug experiment the Enthalpy of the gas remains constant. Hence

$$H = U + PV \text{ is constant}$$

$$dH = dU + P dV + V dP = 0 \quad \dots(1)$$

$$\text{But } T dS = dU + P dV \quad \dots(2)$$

$$\therefore T dS + V dP = 0 \quad \dots(3)$$

Consider  $S$  as a function of  $T$  and  $P$

$$dS = \left( \frac{\partial S}{\partial T} \right)_P dT + \left( \frac{\partial S}{\partial P} \right)_T dP \quad \dots(4)$$

From (3) and (4)

$$T \left( \frac{\partial S}{\partial T} \right)_P dT + T \left( \frac{\partial S}{\partial P} \right)_T dP + V dP = 0 \quad \dots(5)$$

$$\text{But } T \left( \frac{\partial S}{\partial T} \right)_P = \left( T \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial Q}{\partial T} \right)_P = C_P \quad \dots(6)$$

$$\text{From Maxwell's equation, we have } \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P$$

$$\text{From (5), (6), (7) we have } C_P dT + T \left( \frac{\partial V}{\partial T} \right)_P dP + V dP = 0$$

$$C_P dT + \left[ T \left( \frac{\partial V}{\partial T} \right)_P + V \right] dP = 0 \quad C_P dT + \left[ T \left( \frac{dV}{dT} \right)_P + V \right] dP$$

$$\therefore \left( \frac{\partial T}{\partial P} \right)_H = \left[ \frac{T \left( \frac{\partial V}{\partial T} \right)_P + V}{C_P} \right]$$

This is Joule-Thomson equation for cooling.

In this equation  $\left( \frac{\partial T}{\partial P} \right)_H$  is called Joule-Thomson or Joule-Kelvin coefficient.

$$\text{Also } \left( \frac{\partial T}{\partial P} \right)_H = \frac{V}{C_P} \left[ \frac{T}{V} \frac{\partial V}{\partial T} + 1 \right] = \mu$$



**Study Material**

When  $C_p$  correspond to the specific heat at constant pressure, volume for 1 gram of the gas  $\mu$  is called Joule-Thomson coefficient.

Joule-Kelvin effect in the case of ideal gas and real gases

**i) For an ideal gas :**

$$PV = RT$$

$$PdV + VdP = RdT$$

To obtain  $\left(\frac{\partial V}{\partial T}\right)_P$ ,  $dP = 0$  and here  $PdV = RdT$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} = \left(\frac{PV}{T} \frac{1}{P} = \frac{V}{T}\right) \left(\ominus R = \frac{PV}{T}\right)$$

$$\text{From equation } \left(\frac{\partial T}{\partial P}\right)_H = \left[ \frac{T \left(\frac{\partial V}{\partial T}\right)_P - V}{C_P} \right]$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{T \frac{V}{T} - V}{C_P} = \frac{V - V}{C_P} = 0$$

Hence in the case of ideal gas the Joule-Thomson effect is zero.

**ii) For real Gases :** In the case of real gases obeying vander Walls equation, we have

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad PV + \frac{a}{V} - bP - \frac{ab}{V^2} = RT \text{ as } \frac{ab}{V^2} \text{ is negligible}$$

$$PV + \frac{a}{V} - bP = RT \quad PV = RT + bP - \frac{a}{V} \quad \dots(1)$$

The internal work done by the gas for a small change in volume  $dV$  is equal to  $\left(\frac{a}{V^2}\right) dV$ . The internal work done by the gas as the volume of the gas changes from  $V_1$  to  $V_2$ ,

$$= \int_{V_1}^{V_2} \frac{a}{V^2} dV = a \left[ \frac{1}{V} \right]_{V_1}^{V_2} = \left[ \frac{a}{V_1} - \frac{a}{V_2} \right] \quad \dots(2)$$

$$\text{External work done by the gas} = P_2 V_2 - P_1 V_1 \quad \dots(3)$$

$$\text{Total workdone by the gas} = P_2 V_2 - P_1 V_1 + \frac{a}{V_1} - \frac{a}{V_2} \quad \dots(4)$$

From the equations (1) and (4)

$$\begin{aligned} \text{Total work done by the gas} &= R(T_2 - T_1) + b(P_2 - P_1) + \frac{2a}{V_1} - \frac{2a}{V_2} \\ &= RdT + bdP + \frac{2a}{V_1} - \frac{2a}{V_2} \quad \dots(5) \end{aligned}$$

Assuming the gas obeys ideal gas equation

$$P_1 V_1 = RT ; P_2 V_2 = RT ; \frac{1}{V_1} = \frac{P_1}{RT}, \frac{1}{V_2} = \frac{P_2}{RT}$$

$$2a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) = 2a \left( \frac{P_1 - P_2}{RT} \right) = \frac{2a(-dP)}{RT}$$

$$\text{Total work done by the gas} = RdT + bdP - \frac{2adP}{RT} \quad \dots(6)$$

The fall of temperature in  $dT$ , the quantity of heat lost is  $C_v dT$

From the principle of conservation of energy

$$RdT + bdP - \frac{2adP}{RT} + C_v dT = 0$$

$$(C_p - C_v) dT + bdP - \frac{2a}{RT} dP + C_v dT = 0 \quad (\because C_p - C_v = R)$$

$$\therefore C_p dT = \left( \frac{2a}{RT} - b \right) dP \quad \frac{dT}{dP} = \frac{\left( \frac{2a}{RT} - b \right)}{C_p} \quad \dots(7)$$

$$\text{From the equation (7) } \frac{dT}{dP} = 0 \text{ when } \frac{2a}{RT} = b ; T = \frac{2a}{Rb}$$

This temperature of gas at which there is no change of temperature during Joule's expansion is called the temperature of inversion.

From the equation (7) when  $\frac{2a}{Rb} > b$  and as  $dP$  is negative, there is the Cooling effect.

Hence  $T < \frac{2a}{Rb}$  to produce heating effect.

Also when  $\frac{2a}{Rb} < b$  as  $dP$  is negative there is heating effect.

Hence  $T > \frac{2a}{Rb}$  to produce heating effect.

When the temperature of gas is above the temperature inversion there is heating effect during throttle expansion. Also when the temperature of the gas is below the temperature of inversion there is cooling effect during throttle expansion. Hence to produce cooling during the throttle expansion, the gas should possess the temperature less than the temperature of inversion of the gas.

### SHORT ANSWER QUESTIONS

**Q. 4. Define thermodynamic potentials.? Using this derive clausius - clapeyron's equations and gives applications of clausius - clapeyron equation ?**

**Ans :** The Clausius-Clapeyron's latent heat equation relates the change in melting point or boiling point with change in pressure. The equation can be derived from Maxwell's second thermodynamic relation which is expressed as



$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T$$

Multiplying both sides by  $T$ , we have

$$T\left(\frac{\partial P}{\partial T}\right)_v = T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{T \partial S}{\partial V}\right)_T \quad (T = \text{constant})$$

$$= \left(\frac{\partial Q}{\partial V}\right)_T \quad (\text{Second law of thermodynamics})$$

Here  $\partial Q$  represents the heat absorbed at constant temperature. i.e.,  $\partial Q$  is latent heat. Let unit mass of a substance under constant temperature is converted from one state to another state absorbing an amount of heat  $L$  (latent heat). Suppose the specific volumes in the first and second states be  $V_1$  and  $V_2$  then  $\partial V = V_2 - V_1$ . Hence

$$T\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{L}{(V_2 - V_1)}\right)_T \quad \text{or} \quad T\left(\frac{\partial P}{\partial T}\right) = \frac{L}{(V_2 - V_1)}$$

$$\frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}$$

This is Clausius-Clapeyron latent heat equation.

#### Applications of Clausius-Clapeyron Equation :

1. This equation can be used to study the variation of boiling point of a liquid with pressure. When a liquid boils, i.e., changes from liquid state to gaseous state, there is an increase in volume ( $V_2 > V_1$ ). As  $(V_2 - V_1)$  is a positive quantity  $dP/dT$  is also a positive quantity. This means that the boiling point of a liquid rises with increase in pressure or vice versa. This also indicates that under reduced pressure, a liquid boils at lower temperature.

2. This equation can be used to study the variation of melting point of a solid with pressure. This is classified into two classes.

a) When  $V_2 > V_1$  (As for wax and sulphur). In this case  $(dP/dT)$  is a positive quantity. This means the melting point of such substances rise with increase in pressure.

b) When  $V_2 < V_1$  (As for ice, gallium and Bismuth). In this case  $(dp/dT)$  is a negative quantity. This means that the melting point of such substances decrease with increase in pressure.

3. The equation also explains the regelation of ice. When the two pieces of ice are pressed together, they form a single piece. This phenomenon is known as regelation. We know that melting point of ice is lowered with increase in pressure. When between the two surfaces in contact. On removing the pressure, the original melting point is restored. Now water film is frozen and the two pieces form a single ice piece.

#### Q. 5. Define specific heat of Materials ? Deduce the relation between specific heat $C_p - C_v$ ?

**Ans : Concept of specific heats :** Consider a gas of mass  $m$  at a pressure  $P$  and volume  $V$ . If the gas is compressed, there is rise in temperature. In this case, no heat has been supplied to the gas to raise its temperature.

$$\therefore \text{Specific heat, } C = \frac{Q}{m\theta} \quad \text{But } Q = 0 ; C = 0$$

On the other hand, if heat is supplied to the gas and the gas is allowed to expand such that there is no rise of temperature, then

$$C = \frac{Q}{m\theta}$$

Here  $Q = 0 \quad \therefore \frac{Q}{m \times \theta} = \infty$

Thus, the specific heat of a gas varies from zero to infinity.

In order to fix the value of the specific heat of a gas, the pressure or volume has to be kept constant. Consequently a gas has two specific heats.

1. Specific heat at constant volume  $C_v$

2. Specific heat at constant pressure  $C_p$

$C_v$  : It is defined as the quantity of heat required to raise the temperature of one gram of a gas through  $1^\circ\text{C}$  at constant volume.

$C_p$  : It is defined as the quantity of heat required to raise the temperature of one gram of a gas through  $1^\circ\text{C}$  at constant pressure.

$C_p$  is greater than  $C_v$  : When a gas is heated at constant volume, the heat supplied to the gas is wholly used up to raise its temperature. On the other hand when a gas is heated at constant pressure, a part of the heat is used to raise its temperature and a part is used to do external work to keep the pressure constant.

$$\therefore C_p > C_v$$

**Relation between  $C_p$  and  $C_v$  :**

We know,  $C_p = \left( \frac{\partial Q}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p \left[ \because dS = \frac{dQ}{T} \right]$  and  $C_v = \left( \frac{\partial Q}{\partial T} \right)_v = T \left( \frac{\partial S}{\partial T} \right)_v$

Let us consider  $S$  as a function of temperature and volume

$$dS = \left( \frac{\partial S}{\partial T} \right)_v dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

Differentiating the above with temperature at constant pressure, we get

$$\left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial S}{\partial T} \right)_v + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_p$$

But from Maxwell's relations  $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_v$

Substituting equation (18) (17) we get

$$\left( \frac{\partial S}{\partial T} \right)_p = \left( \frac{\partial S}{\partial T} \right)_v + \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

Multiplying above equation (19), by  $T$  on both sides we get

$$T \left( \frac{\partial S}{\partial T} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_v + T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

Substituting equations (15) and (16) in equation (20), we get

$$\therefore C_p = C_v + T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

$$\therefore C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$



$$\text{or } C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

This is the required relation between  $C_p$  and  $C_v$ .

$C_p - C_v = R$  for an ideal gas : For ideal gas,  $PV = RT$

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{TR}{V} \text{ and } \left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{P}$$

$$\text{But } C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p \text{ (from equation 21)}$$

$$\text{Substituting equation (22) in (21) we get } C_p - C_v = T \left( \frac{R}{V} \right) \left( \frac{R}{P} \right)$$

$$= \frac{TR^2}{PV} = \frac{TR^2}{RT} (\because PV = RT) = R$$

$$\therefore C_p - C_v = R$$

**Relation between  $C_p$  and  $C_v$  for a gas obeying vander wall's equation :**

For a gas obeying vander wall's equation

$$\left( P + \frac{a}{V^2} \right) (v - b) = RT \quad \text{or} \quad \left( P + \frac{a}{V^2} \right) = \frac{RT}{V - b}$$

Differentiating above equation with respect to  $T$  at constant volume  $V$ , we get

$$\left( \frac{\partial P}{\partial T} \right)_v = \frac{R}{V - b}$$

Differentiating equation (24) with respect to  $T$  at constant pressure  $P$ , we obtain

$$\frac{2a}{V^3} \left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{(V - b)} - \frac{RT}{(V - b)^2} \left( \frac{\partial V}{\partial T} \right)_p \quad \text{or} \quad \left( \frac{\partial V}{\partial T} \right)_p = \frac{\frac{R}{V - b}}{\frac{RT}{(V - b)^2} - \frac{2a}{V^3}}$$

$$\text{From equation (21) we have } C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial V}{\partial T} \right)_p$$

Substituting equations (25) and (26) we get

$$C_p - C_v = \frac{T \left( \frac{R}{V - b} \right) \left( \frac{R}{V - b} \right)}{\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right]} = \frac{\frac{RT}{(V - b)^2} \cdot R}{\left[ \frac{RT}{(V - b)^2} - \frac{2a}{V^3} \right]}$$

$$C_p - C_v = \frac{R}{\left[ \frac{1 - 2a(V - b)^2}{V^3 RT} \right]}$$

Neglecting "b" as compared to  $V$ , we get

$$C_p - C_v = \frac{R}{1 - \frac{2a}{VRT}} = R \left( 1 + \frac{2a}{VRT} \right)$$

Expanding (28) by binominal theorem and remembering that  $a$  is small we get

$$C_p - C_v = R \left( 1 + \frac{2a}{VRT} \right)$$

Where  $R$  is in heat units.

**Q. 6. Define Specific heat of materials ? Derive the expression for ratio of two specific heats  $C_p/C_v$ ?**

**Ans :** The specific heat of a substance is essentially the amount of heat required to raise the temperature of unit mass of the substance through  $1^\circ\text{C}$ . In case of solids and liquids, the change of volume and hence, the external work done during the change of temperature is negligible small and hence, there is only one specific heat in case of solids and liquids. We know that gases suffer big changes of pressure and volume during the change of temperature. Thus, it is important to state the condition under which the heat is supplied. In case of gases, generally, heat is supplied under the following two conditions :

i) at constant volume, and ii) at constant pressure

**Specific heat at constant volume  $C_v$  :** The specific heat at constant volume is the amount of heat required to raise the temperature of one gram gas through  $1^\circ\text{C}$  when the volume of gas is kept constant.

**Specific heat at constant pressure  $C_p$  :** The specific heat at constant pressure is the amount of heat required to raise the temperature of 1 gram gas through  $1^\circ\text{C}$  when the pressure is kept constant.

**Ratio of two specific heats :** Here we shall obtain the ratio  $(C_p/C_v) = \gamma$ , using Maxwell's relations.

The coefficient of volume elasticity is defined by

$$E = \frac{\text{Stress}}{\text{Volume strain}} = - \frac{dP}{dV/V} = -V \frac{dP}{dV}$$

Therefore, the adiabatic elasticity  $E_s$  (entropy constant) and isothermal elasticity  $E_T$  (temperature constant) are given by

$$E_s = -V \left( \frac{\partial P}{\partial V} \right)_s \quad \dots(1)$$

$$\text{and} \quad E_T = -V \left( \frac{\partial P}{\partial V} \right)_T \quad \dots(2)$$

Dividing the two equations, we get

$$\frac{E_s}{E_T} = \frac{(\partial P / \partial V)_s}{(\partial P / \partial V)_T} = \frac{\left( \frac{\partial P}{\partial T} \frac{\partial T}{\partial V} \right)_s}{\left( \frac{\partial P}{\partial S} \frac{\partial S}{\partial V} \right)_T} = \frac{\left( \frac{\partial P}{\partial T} \right)_s \left( \frac{\partial T}{\partial V} \right)_s}{\left( \frac{\partial P}{\partial S} \right)_T \left( \frac{\partial S}{\partial V} \right)_T}$$

Substituting the values from Maxwell's relations, we have

$$\frac{E_s}{E_T} = \frac{\left( \frac{\partial S}{\partial V} \right)_P \left( \frac{\partial P}{\partial S} \right)_V}{\left( \frac{\partial T}{\partial V} \right)_P \left( \frac{\partial P}{\partial T} \right)_V} = \frac{\left( \frac{\partial S}{\partial V} \right)_P}{\left( \frac{\partial T}{\partial V} \right)_P} \frac{\left( \frac{\partial P}{\partial S} \right)_V}{\left( \frac{\partial P}{\partial T} \right)_V}$$



$$= \left( \frac{\partial S}{\partial T} \right)_p \left( \frac{\partial T}{\partial S} \right)_p = \left( \frac{\partial S}{\partial T} \right)_p / \left( \frac{\partial S}{\partial T} \right)_p$$

Multiplying the numerator and denominator by  $T$ , we get

$$\frac{E_s}{E_v} = \frac{T \left( \frac{\partial S}{\partial T} \right)_p}{T \left( \frac{\partial S}{\partial T} \right)_v} = \frac{\left( \frac{\partial Q}{\partial T} \right)_p}{\left( \frac{\partial Q}{\partial T} \right)_v} \quad (\ominus T \partial S = \partial Q)$$

But  $\left( \frac{\partial Q}{\partial T} \right)_p = C_p$  and  $\left( \frac{\partial Q}{\partial T} \right)_v = C_v$

$$\frac{C_p}{C_v} = \gamma = \frac{E_s}{E_v}$$

Thus, the ratio of specific heats of the substance at constant pressure and at constant volume is equal to the ratio of adiabatic and isothermal elasticities.

**Q. 7. Explain the importance of thermodynamical functions ?**

**Ans :** Thus, the four thermodynamical potentials, i.e.,  $U(S, T)$ ;  $F(T, V)$ ;  $H(S, P)$  and  $G(T, P)$  lead us to the four thermodynamical relations known as Maxwell's relations.

**Importance of the thermodynamical functions :** Thermodynamic functions are of practical importance in studying the conditions of equilibrium of a system. The internal energy is an extensive property. Its value is proportional to the quantity of matter constituting the system under consideration. The change in internal energy, when a system passes from one state to other, is independent of the path followed between the two states.

The condition of equilibrium for a process in which temperature and volume of the system remain constant (isothermal - isochoric process) may be expressed as

$$dF = 0 \quad (\ominus dF = -P dV - S dT)$$

So in isothermal - isochoric process only those states are stable in which the Helmholtz free energy is a minimum (not maximum). We have shown that Helmholtz free energy in any process at constant temperature is equal to the reversible work done by the system  $[-dF = dW]$

We know that reversible work done is the maximum work which can be obtained from the given change in state. Thus, in an isothermal process, the decrease in Helmholtz free energy is a measure of the maximum work obtainable from the change in state.

Enthalpy is an extensive property of the system. The change in enthalpy is equal to the quantity of heat given to the system for the change of state at constant pressure.

Gibb's free energy  $G$  is also a characteristic property of the system. It depends upon the thermodynamic state of the system. In an isothermal-isobaric process (Temperature and pressure constant)  $dG = 0$ , which means that Gibb's function  $G$  is a minimum.

### SOLVED PROBLEMS

**Q. 1. Calculate the depression of freezing point for water for an increase of pressure of 1 atmosphere.**

**Sol :** Specific volume of ice  $V_1 = 1.09 \text{ cc}$

Specific volume of water  $V_2 = 1.00 \text{ cc}$

Since  $\frac{\partial P}{\partial T} = \frac{L}{T(V_2 - V_1)}$  where  $L$  is expressed in ergs.

Also  $\frac{\partial P}{\partial T} = \frac{LJ}{T(V_2 - V_1)}$  where is expressed in calories and

$4.2 \times 10^7$  ergs/Calories

$$\therefore \partial T = \frac{T dP (V_2 - V_1)}{LJ} = \frac{273 \times 76 \times 13.6 \times 980 (1 - 1.09)}{80 \times 4.2 \times 10^7} = \frac{-0.09 \times 273 \times 76 \times 13.6 \times 980}{80 \times 4.2 \times 10^7}$$

$$= -0.0074^\circ\text{C per atmosphere.}$$

Q. 2. Calculate the elevation of boiling point of water for an increase of pressure of 1 cm of mercury.

Sol : Specific volume of water = 1.0 cc    Specific volume of steam = 1677 cc

Boiling point of water =  $100^\circ\text{C}$

Latent heat of vapourisation of water =  $L = 539 \text{ cal/gm}$

$$dT = \frac{(V_2 - V_1) T dP}{L} \text{ when } L, \text{ is in ergs}$$

$$dT = \frac{(V_2 - V_1) T (dP)}{LJ} \text{ where } L \text{ is in calories} = \frac{(1677 - 1) 373 \times 1 \times 13.6 \times 980}{539 \times 4.2 \times 10^7}$$

$dT = 0.3681^\circ\text{C per cm of mercury.}$

Q. 3. Deduce the change in the boiling point of water when the pressure is changed by 1 cm of mercury ( $L_s = 2.268 \times 10^6 \text{ J kg}^{-1}$ )

Sol :  $dp = 1 \text{ cm of Hg} = 10^{-2} \times (13.6 \times 10^3) \times 9.8 = 13.6 \times 98 \text{ Nm}^{-2}$

Volume of 1 kg of water ( $V_1$ ) =  $1000 \text{ c.c} = 10^{-3} \text{ m}^3$

Volume of 1 kg of steam ( $V_2$ ) =  $1.674 \text{ m}^3$

From Clausius - Clayperon equation  $\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$

$$dT = \frac{T dP (V_2 - V_1)}{L} = \frac{373 \times 13.6 \times 98 (1.674 - 0.001)}{2.268 \times 10^6} = 0.3667 \text{ K}$$

Change in boiling point of water =  $0.3667 \text{ K}$

Q. 4. Calculate the change in melting point of ice under a pressure of 100 atmospheres.

(Density of ice =  $0.0917 \text{ gm/c.c.}$ ,  $L_1 = 336 \text{ J/gm}$ )

Sol : Pressure  $dp = 100 \text{ atmosphere} = 100 \times 1.03 \times 10^5 \text{ N/m}^2$

Latent heat,  $L = 336 \text{ J/gm} = 336000 \text{ J/kg}$

Initial volume  $\frac{dP (V_2 - V_1)}{L}$

Final Volume  $V_2 = \frac{1}{10^3} \text{ m}^3 / \text{kg}$

From Clausius - Clayperon equation  $dT = \frac{dP \times T \times (V_2 - V_1)}{L}$

$$= \frac{(76 \times 136 \times 980) (273) \left( \frac{1}{1000} - \frac{1}{917} \right)}{336000} = -0.0714 \text{ K}$$

—O—



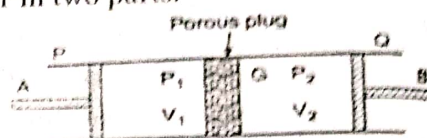
## UNIT - IV LOW TEMPERATURE PHYSICS

### LONG ANSWER QUESTIONS

**Q.1. Describe Joule-Thomson porous plug experiment. What are the important inferences from this experiment.**

**Ans : Description :** The principle of Joule-Kelvin experiment is shown in fig.  $PQ$  is thermally insulated cylinder containing porous plug (porous material such as cotton wool) and fitted with two nonconducting pistons  $A$  and  $B$ . The porous plug separates the cylinder in two parts.

The gas is compressed to a high pressure  $P_1$  on one side. The gas then passes through the porous plug on the other side. There is a constant lower pressure  $P_2$ . When the compressed gas molecules come towards the lower pressure side after pass



Fig

ing through porous plug, they are drawn apart and hence, suffer a change in temperature. The change in temperature is called as Joule-Thomson effect.

This effect may be stated as follows :

*When a gas under a constant pressure is passed through a porous plug to a region of low it constant pressure, the gas suffers a change in temperature. Such a change was actually demonstrated by Joule and Kelvin and hence, known as Joule-Kelvin or Joule-Thomson effect.*

#### **Results of Joule-Kelvin Effect (Conclusion)**

1. All gases suffer a change in temperature after passing through the porous plug.
2. At ordinary temperatures all gases except hydrogen and helium show cooling effect. For example, at  $0^\circ\text{C}$  hydrogen shows a heating of  $0.04^\circ\text{C}$  per atmospheric pressure difference.
3. The change in temperature is directly proportional to the difference in pressure on the two sides of the porous plug.
4. The fall in temperature per atmospheric difference of pressure decreases as the initial temperature of the gas is raised. It becomes zero at a particular temperature which is different for different gases. Above this temperature, instead of cooling, heating is observed. The particular temperature at which Joule-Kelvin effect changes the sign is called as temperature of inversion.

Thus, every gas below its temperature of inversion will cool on passing through porous plug. The inversion temperature of hydrogen is  $-80^\circ\text{C}$ . so if it is pre-cooled to a temperature less than  $-80^\circ\text{C}$  and then passed through the porous plug, it suffers cooling.

Referring to fig., consider unit mass of a gas in the left compartment. Now suppose that the piston  $A$  is moved towards the porous plug. The result is that a certain mass of the gas is transferred from left compartment (high pressure side) to right compartment (low pressure side). Here it is assumed that the high pressure in left compartment and low pressure on right compartment are kept constant because the compartments are thermally insulated and the piston is moved very slowly.

Let  $P_1$ ,  $V_1$  and  $T_1$  represent pressure, volume and temperature respectively on high pressure side and  $P_2$ ,  $V_2$  and  $T_2$  similar quantities on low pressure side. Let  $U_1$  and  $U_2$  be the internal energies of unit mass of the of the gas before and after passing through porous plug.

Work done on the gas by piston  $A = P_1 V_1$

Work done by the gas on piston  $B = P_2 V_2$

Net work done by the gas =  $(P_2 V_2 - P_1 V_1)$ .

As the system is thermally isolated, this work must have been done at the expense of the internal energy of the gas. Hence,

$$P_2 V_2 - P_1 V_1 = U_1 - U_2$$

or  $U_1 + P_1 V_1 = U_2 + P_2 V_2 = \text{constant}$

The quantity  $U + PV$  is known as "enthalpy". Thus, in Joule-Kelvin effect, the initial and final enthalpies are equal, i.e., the enthalpy remains constant.

$$U + PV = \text{constant}$$

Now we shall discuss the behaviour of gases at different temperatures.

### Perfect Gas

In case of a perfect gas Boyle's law is obeyed, i.e.,  $P_1 V_1 = P_2 V_2$ , hence,

$$U_1 = U_2$$

If  $K_1$  and  $\rho_1$  be the kinetic and potential energies of the gas on left hand side respectively and  $K_2$  and  $\rho_2$  similar quantities on right hand side, then

$$K_1 + \rho_1 = K_2 + \rho_2$$

We know that there is no force of attraction between the molecules of a perfect gas and hence,  $\rho_1 = \rho_2 = 0$ . Thus,

$$K_1 = K_2$$

or  $T_1 = T_2$

Therefore, the Joule-Kelvin effect is zero for a perfect gas.

### Real Gases :

For real gases  $P_1 V_1 \neq P_2 V_2$ . So the net external work done by the gas  $P_2 V_1 + P_1 V_2 \neq 0$ . Therefore, there are three cases to be considered depending upon the initial temperatures (

- i) **Below the Boyle temperature** : Experiments show that below Boyle's temperature, the product  $PV$  decreases as the pressure  $P$  increases upto a moderate value, i.e.,

$$P_2 V_2 > P_1 V_1$$

$$U_1 > U_2$$

$$(\ominus P_1 V_1 + U_1 = P_2 V_2 + U_2)$$

Thus, on passing through porous plug, the internal energy of the gas will decrease and hence, the temperature falls (cooling effect).

- ii) **At Boyle's temperature** : At Boyle's temperature, the gas strictly obey Boyle's law, i.e., the product  $PV$  remains constant. Thus,

$$P_2 V_2 = P_1 V_1$$

$$U_1 = U_2$$

$$(\ominus P_1 V_1 + U_1 = P_2 V_2 + U_2)$$

i.e., the internal energy remains unchanged or the temperature of the gas remains constant.

- iii) **Above Boyle's temperature** : The product  $PV$  increases as the pressure increases, i.e.,  $PV$  is smaller at lower pressure than at high pressure or

$$P_1 V_1 > P_2 V_2$$

or  $U_2 > U_1$

Thus, the internal energy of the gas will increase and hence, its temperature will rise (heating effect).

**Q. 2. What is Joule-Kelvin effect? Obtain an expression for the cooling produced due to this effect?**

**Ans :** Consider a thermally insulated cylinder AB divided into two compartments by a porous plug G. Let  $V_1$  and  $V_2$  be the volumes of the gas before and after passing through the porous plug respectively. External work done on the gas by the piston =  $P_1 V_1$



External work done by the gas on the piston =  $P_2 V_2$

Net external work done by the gas =  $(P_2 V_2 - P_1 V_1)$

The internal work done against the forces, when one gram mole expands from volume  $V_1$  to volume  $V_2$  is

$$\int_{V_1}^{V_2} \left( \frac{a}{V^2} \right) dV = \frac{a}{V_1} - \frac{a}{V_2}$$

Total work done by the gas

$$W = (P_2 V_2 - P_1 V_1) + \frac{a}{V_1} - \frac{a}{V_2} \quad \dots (1)$$

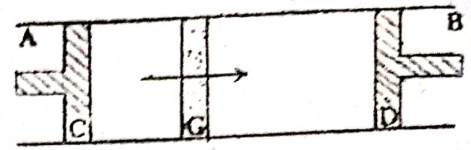


Fig.

According to Vander Wall's equation, we have  $\left( P + \frac{a}{V^2} \right) (V - b) = RT$

As  $a$  and  $b$  are small quantities,  $\frac{ab}{V^2}$  can be neglected

$$PV + \frac{a}{V} - Pb = RT \text{ (or) } PV = RT - \frac{a}{V} + Pb \text{ and } P_2 V_2 = RT - \frac{a}{V_2} + P_2 b$$

$$\therefore (P_2 V_2 - P_1 V_1) = a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) - b (P_1 - P_2) \quad \dots (2)$$

From equations (1) and (2), we get  $W = a \left( \frac{1}{V_1} - \frac{1}{V_2} \right) - b (P_1 - P_2) + \frac{a}{V_1} - \frac{a}{V_2}$

$$W = 2 \left( \frac{1}{V_1} - \frac{1}{V_2} \right) - b (P_1 - P_2) \quad \dots (3)$$

As  $a$  and  $b$  are very small quantities  $PV = RT$  (or)  $\frac{1}{V} = \frac{P}{RT}$

$$\therefore \frac{a}{V_1} = \frac{P_1 a}{RT} \text{ and } \frac{a}{V_2} = \frac{P_2 a}{RT} \quad \dots (4)$$

Substituting in the equations (3)

$$W = 2 \left( \frac{P_1 a}{RT} - \frac{P_2 a}{RT} \right) - b (P_1 - P_2) \quad W = \frac{2a}{RT} (P_1 - P_2) - b (P_1 - P_2) \quad \dots (5)$$

$$\therefore W = (P_1 - P_2) \left( \frac{2a}{RT} - b \right)$$

As the system is thermally insulated, this work is drawn from the K.E. of the molecules of the gas. Hence the gas cools. Let  $dT$  be the fall in temperature.

If  $C_p$  be the specific heat at constant pressure, then the amount of heat that must be supplied to restore the original temperature will be  $C_p dT$  calories (or)  $C_p dT J$  ergs.

$$\therefore C_p dT = [P_1 - P_2] \left( \frac{2a}{RT} - b \right) \quad \dots (6)$$

If  $P_1 - P_2 = dP$  (change in pressure)

$$\therefore \frac{dT}{dP} = \frac{\left( \frac{2a}{RT} - b \right)}{C_p J} \quad \dots (7)$$

Cases :

1. If  $\left( \frac{2a}{RT} \right) > b$ , then  $dT = +ve$  and there will be a cooling effect because  $dT$  represents fall in temperature.
2. If  $\left( \frac{2a}{RT} \right) < b$ , then  $dT = -ve$  and there will be a heating effect.
3. If  $\left( \frac{2a}{RT} \right) = b$ , then  $dT = 0$  then will be no effect.

The temperature at which joule-Thomson effect is zero and changes sign is known as the "Temperature of inversion" ( $T_i$ ).

$$\therefore \frac{2a}{RT_i} = b \text{ (or) } T_i = \left( \frac{2a}{Rb} \right)$$

In equation (7) the  $\frac{dT}{dP}$  represents, the change in temperature due to change in pressure and is referred to as "Joule Kelvint Coefficient" (or) "differential Joule-Kelvin effect".

**Q.3. Explain what is meant by Adiabatic demagnetization? How it is achieved in practice ? Discuss the result obtained?**

**Ans : Definition :** In a paramagnetic substance, the elementary molecular magnets inside it all lie in a disorderly fashion. They form neutralizing groups so that their net effect is zero. When we magnetise such a substance, these groups of dipoles get broken up and get arranged in an orderly manner parallel to the field applied. Work is done on the substance and this appears in the form of heat. So its temperature rises. The stronger the magnetisation, the greater the rise in temperature. If we demagnetise the substance, the properly aligned dipoles in it, again get back to their enutralising disorderly state. in the process, work is done by the substance, with the result that if it be in thermal isolation from its surroundings the necessary energy for this work is drawn from the substance itself and its temperature, therefore, falls. This is known as 'adiabatic demagnetisation'.

**Method :** The specimen is a single crystal, or a mixture of small crystals or in the form of powder. It is either suspended or placed on a thin glass pedestal, inside a glass bulb B. Bulb B can be supplied with helium gas, or evacuated by a diffusion pump as desired, is surrounded by Dewar

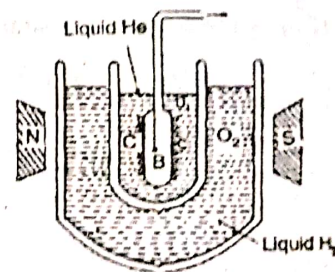


Fig.



flasks  $D_1$  and  $D_2$  containing liquid helium and liquid hydrogen respectively. The entire assembly is placed in between the pole pieces  $N$  and  $S$  of a powerful magnet.

Helium gas is introduced in the bulb  $B$  which helps to have thermal contact of the specimen, kept in it, with the liquid in  $D_1$  so that it may acquire the temperature of the latter. This temperature lies between  $1.2$  and  $1.5$  K, depending upon the pressure. Thus, the helium gas introduced merely serves as a conductor of heat to enable the specimen to attain temperature equilibrium rapidly. It is referred as the exchange gas. The current of electromagnet is then switched on. This produces a magnetic field of order of  $10^4$  oersted at the specimen. The specimen is thus magnetised. The heat produced in the specimen, during magnetization, is conducted away by the exchange gas in  $B$  to the liquid helium in  $D_1$ . Here the specimen in  $B$  is left both cold and highly magnetised. The exchange gas in  $B$  is now thermally isolated from  $D_1$  and  $D_2$ . The current is, switched off, thus cutting off the magnetic field. This results in the specimen getting almost instantaneously demagnetised adiabatically, and its temperature falls.

**Theory :** When an external magnetic field is applied on a paramagnetic substance, the molecules present in it try to align in the direction of field. This is due to work done on the molecules. Let ' $B$ ' be the magnetic induction field strength applied on the paramagnetic substance. Then the intensity of magnetisation changes by an amount  $dI$

Work done by the field  $= BdI$ .

When the substance is demagnetised, work done by the substance  $= - BdI$

We know from first law of thermodynamics  $dQ = dU + dW$

$$dQ = dU + (PdV - BdI) \quad \dots (1)$$

Here the process is carried at constant volume. So the change in volume  $dV = 0$ .

From (1) we can write  $dQ = dU - BdI$

But change in entropy  $dS = \frac{dQ}{T}$

$$dQ = TdS \quad TdS = dU - BdI$$

But from maxwells thermodynamical relation, we know that  $\left[ \frac{\partial T}{\partial P} \right]_S = - \left[ \frac{\partial V}{\partial S} \right]_P$

Here put  $-B$  for  $P$  and  $I$  for  $V$   $\left[ \frac{\partial T}{\partial P} \right]_S = - \left[ \frac{\partial V}{\partial S} \right]_P \quad \dots (2)$

If  $m$  is the mass of substance,  $C$  is the specific heat at constant magnetic induction fixed, then

$$\partial Q = m C_1 \partial T$$

$$\therefore \left[ \frac{\partial Q}{\partial T} \right] = mC_1$$

We know  $\partial S = \frac{\partial Q}{T}$

$$\therefore \left[ \frac{\partial S}{\partial T} \right]_B = \frac{1}{T} \left[ \frac{\partial Q}{\partial T} \right] = \frac{mC_1}{T}$$

By substituting this value in equation (2) we get

$$\therefore \partial T = + \frac{T}{mC_1} \left[ \frac{\partial I}{\partial T} \right]_B \partial B \quad \dots (3)$$

The above equation represents the fall in temperature of the substance due to Adiabatic demagnetisation. The magnetic susceptibility of a substance is defined as the ratio of intensity of magnetisation of specimen to the intensity of magnetising field.

$$\psi = \frac{1}{B} \quad \dots (4)$$

According Curie law, the susceptibility is inversely proportional to absolute temperature.

$$\psi = \frac{1}{T} \therefore \psi = \frac{C}{T} \quad \dots (5)$$

Here C is a constant

$$\therefore \frac{1}{B} = \frac{C}{T} \quad \therefore I = \frac{BC}{T}$$

By substituting this I value in equation (3)

$$\therefore \partial T = + \frac{T}{mC} \left[ \frac{\partial}{\partial T} \left( \frac{C_1 B}{T} \right) \right] \partial B \quad \dots (6)$$

Let  $T_1$  and  $T_2$  be the initial and final temperatures of the substance,  $B_1$  and  $B_2$  are the initial and final magnetic induction field strengths respectively.

$$\int_{T_1}^{T_2} \partial T = \frac{T}{mC} \int_{B_1}^{B_2} \frac{\partial}{\partial T} \left( \frac{C_1 B}{T} \right) \partial B$$

$$\therefore T_2 - T_1 = + \frac{TC_1}{mC} \left[ \frac{B^2}{2} \right]_{B_1}^{B_2} \left( - \left[ \frac{1}{T^2} \right] \right) = \frac{C_1}{2mCT} (B_2^2 - B_1^2)$$

When  $B_2 = 0$ , then

$$\therefore T_2 - T_1 = \frac{C_1}{2mCT} B_1^2$$

The -ve sign shows that there is fall in temperature.

### SHORT ANSWER QUESTIONS

**Q. 1. Write the distinction between Adiabatic and Joule Thomson expansion.**

**Ans : Distinction between Adiabatic and Joule Thomson :**

Joule-Thomson expansion	Adiabatic expansion
1. The cooling is mainly due to internal workdone by the gas against intermolecular forces of attraction. That is why, this is also called throttle expansion.	1. The cooling of a gas is mainly due to the external workdone by the gas. For perfect gas also there is cooling.
2. For perfect gas, there is no cooling.	2. For any gas, we can observe cooling effect irrespective of its initial temperature.
3. For a real gas, there is cooling effect, when its initial temperature is below its temperature of inversion.	3. There is no such heating effect.



4. There will be heating effect if the gas is initially above its inversion temperature.	4. There is always cooling effect.
5. Cooling produced per unit fall in pressure is small.	5. Cooling produced per unit fall in pressure is high.
6. It is an isenthalpy process.	6. It is an isentropic process.
7. It is always irreversible.	7. It is reversible.

**Q. 2. Explain the methods for producing Low temperatures.**

**Ans :** The researches of various scientists have conclusively established that the lowest temperature is  $-273^{\circ}\text{C}$ . This is known as the absolute zero of temperature. Low temperatures can be achieved by the following methods.

- 1. Freezing mixtures :** Pure melting ice produces a temperature of  $0^{\circ}\text{C}$ . Still lower temperatures are obtained by freezing mixtures. When common salt is mixed with ice, some of the ice melts in cooling the salt to  $0^{\circ}\text{C}$ . The salt readily dissolves in the water formed from the melting ice. Heat is now absorbed while salt is dissolving in water (heat of solution) and further ice will melt absorbing latent heat of fusion of ice. Thus the temperature falls below  $0^{\circ}\text{C}$ .

A mixture of ice and common salt gives  $-22^{\circ}\text{C}$ , ice and calcium chlorides gives  $-55^{\circ}\text{C}$  and ice potassium hydroxide gives  $-75^{\circ}\text{C}$ .

- 2. Evaporation of liquids at reduced pressure :** When a liquid evaporates it draws the latent heat of evaporation from the surroundings. By reducing the pressure on the liquid surface the liquid can be made to boil at the room temperature, without supply of heat from outside. The latent heat necessary for boiling is taken from the liquid itself and consequently the temperature of the liquid falls.

Easily liquefiable gases boiling under atmospheric pressure given temperature less than  $0^{\circ}\text{C}$ .

- |   |  |
|---|--|
| a) Boiling liquid $\text{SO}_2$ gives $-10^{\circ}\text{C}$ | b) Boiling liquid methychloride gives $-24^{\circ}\text{C}$      |
| c) Boiling $\text{NH}_3$ gives $-33.4^{\circ}\text{C}$      | d) Boiling liquid $\text{CO}_2$ gives $-103.7^{\circ}\text{C}$ . |

Still lower temperatures were obtained after the announcement of the liquefaction of permanent gases. Liquid  $\text{O}_2$  enable to obtain temperature of  $-183^{\circ}\text{C}$ . Liquid  $\text{N}_2$  boiling under normal pressure gives  $-196^{\circ}\text{C}$ , Neon gives  $-246^{\circ}\text{C}$  and  $\text{H}_2$  gives  $-253^{\circ}\text{C}$ . By boiling helium under reduced pressure, a temperature of about  $-272^{\circ}\text{C}$  or  $1^{\circ}\text{K}$  were obtained by adiabatic demagnetisation of paramagnetic salts.

- 3. Adiabatic demagnetisation :** When a paramagnetic substance is magnetised, external work is done on it. This results in a rise of temperature. Similarly, when it is demagnetised (under adiabatic conditions) the temperature falls. This principle was utilised by Giauque, Debye and others in producing very low temperatures below  $1^{\circ}\text{K}$ .

**Q. 3. Explain the principle of regenerative cooling.**

**Ans :** The cooling produced in Joule-Thomson expansion of a gas depends on the difference of pressure on the two sides of the porous plug and the initial temperature. For most of the gases the Joule-Thomson cooling is a very small. However, the cooling effect can be intensified by employing the process called the regenerative cooling.

In this method a portion of the gas which suffers Joule-Thomson expansion and becomes cooled is employed to cool other portions of the incoming gas before the latter reaches the nozzle to suffer Joule-Thomson expansion. After suffering the Joule-Thomson expansion at the nozzle, the incoming gas becomes further cooled. By a continuous application of this process, the temperature of



the gas coming out of the nozzle, Falls continuously till the gas starts liquifying on the low pressure side. The commutative process used to cool a gas continuously is called the regenerative cooling.

The arrangement of regenerative principle is shown in Fig. The gas is compressed to a high pressure in the compressor. The heat of compression is removed by passing the gas in a water cooled jacket *A*. Then this gas enters the inner tube of regenerator *R* and suffers Joule-Thomson expansion. This cooled gas returns by the outer tube and absorbs heat from the incoming high pressure gas before it reaches the compressor almost at the same temperature as the incoming gas at *R*. After being compressed and passing through the water cooled jacket, it reenters the regenerator and is further cooled by the outgoing gas which has previously suffered joule-Thomson expansion. Then it suffers Joule-Thomson expansion and hence its temperature further falls. As the process continues the gas approaching the valve *V*

becomes more and more cooled till the Joule-Thomson cooling at *V* is sufficient to liquify the gas. A portion of the escaping gas is condensed in the flask *F*. At this stage the temperature of the whole apparatus becomes steady.

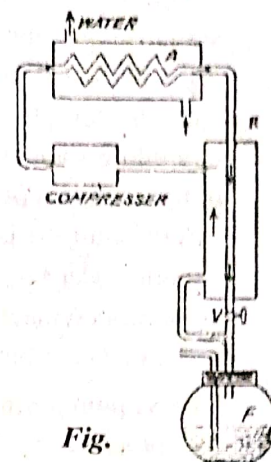


Fig.

#### Q.4. Explain briefly the principle and working of a refrigerator.

**Ans:a) Refrigeration :** Refrigeration is to maintain low temperature surroundings. A machine used for producing low temperature below surroundings and maintaining an enclosure at that temperature called as refrigerator. The liquid used to produce cooling is called refrigerant.

#### Properties of Refrigerant :

1. The refrigerant should have low boiling point and low freezing point.
2. It should be vapour at normal temperature and pressure.
3. It should be non-flammable, non-explosive and should not have bad effect on the stored food material.
4. It should have high thermal conductivity.
5. The latent heat of vapourisation must be large.
6. The specific volume should be small.

**b) Refrigerator :** Refrigerator can be considered to be the heat engine operated in the reverse order. That is the heat engine absorbs heat from a high temperature source converts part of heat into mechanical work output and rejects the difference as heat to a lower temperature sink. But the refrigerator absorbs heat from the low temperature sink, the compressor supplies mechanical work input and the sum is rejected at high temperature source.

From the diagram  $Q_2$  is the heat removed from refrigerator by the cooling coils with in it.  $W$  is the work done by the motor and  $Q_1$  the heat delivered to the external cooling coils and removed by circulating air water.

Hence,  $Q_1 = Q_2 + W$

The Coefficient of performance of a refrigerator is the ratio of heat removed from the refrigerator to the machanical work  $W$  done by the compressor.

$$\text{Coefficient of performance} = K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

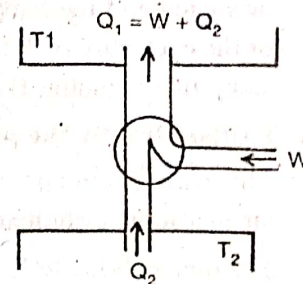


Fig.



Refrigerators are of two types depending upon how the low pressure vapour is compressed. They are vapour compression machine, the vapour absorption machine, the vapour absorption machine, the low pressure vapour is dissolved in a dilute solution of the refrigerant liquid at room temperature and the concentrated solution is heated to expel the vapour under high pressure. The vapour compression machines are more efficient and can easily be operated.

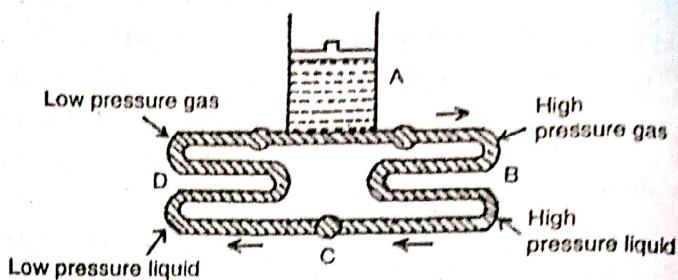


Fig.

**The vapour compression machine :** In this an electric motor works as a compressor and the low pressure vapour like Sulphur dioxide or Freon is compressed. The figure below shows machine.

$P$  is a compression pump worked by means of an electric motor. At its bottom there are two valves  $V_1$  and  $V_2$ . When the piston is pushed downwards the pressure of the vapour under it increases and the valve  $V_1$  opens while the valve  $V_2$  remains closed. The vapour under high pressure enters into the condenser coil  $C$  made of copper. This coil is surrounded by an enclosure containing cold water or a stream of cold water can be circulated through it. The heat of compression is removed by the cold water and the vapour under high pressure and low temperature liquefies in  $C$ .

This liquid refrigerant passes through a valve  $V$  into the refrigerator coil  $R$ . Due to the low pressure in  $R$ ; the liquid evaporates. The pressure in  $R$  can be lowered by using  $P$ . The amount of heat required for evaporation is extracted from the surrounding liquid say water. The water is cooled. As the liquid evaporates, the pressure increases and when  $P$  is raised the vapour opens the valve and enters into the barrel in which the position works. Now when  $P$  is lowered, the vapour opens  $V_1$  and enters into the coil  $C$  so on. Thus as more and more liquid evaporates in  $R$ , more cooling is produced and the temperature of the surrounding water is lowered. After a time the temperature of the enclosure of  $R$  reaches the required low value. An automatic device is used for starting and stopping the motor. By using the thermostat, the temperature can be controlled.

**Q. 5. Explain briefly the principle and working of Air Conditioning Machine.**

**Ans :** The main functioning of an air-conditioning machine is to keep the temperature and humidity of the air in a room or hall at required comfortable levels.

The human body feels comfortable at about  $20^\circ\text{C}$  in winter and below  $25^\circ\text{C}$  in summer. In addition, the relative humidity of the surroundings must be not less than 35% and not more than 75%. To fulfil these requirements, we employ air conditioning. Air conditioning has become a way of life for many of us and new technology makes these systems lighter, more efficient and more environmentally friendly than ever before.

The few basic rules of physics, namely heat transfer, evaporation, condensation and pressure are used in air conditioning machine.

**Parts of air conditioning machine :**

Following are the main parts of an air conditioning machine :

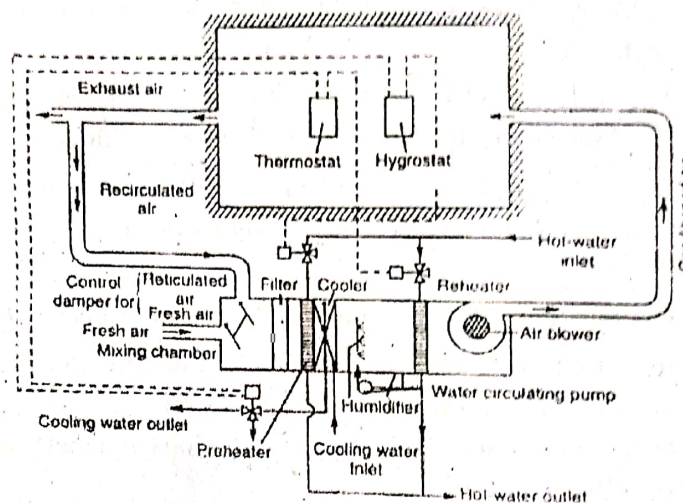
1. Thermostat that controls the temperature.
2. Hygrostat that controls the humidity of air.



3. Control damper that recirculates air and fresh air.
4. Filter that absorbs dust from mixed air.
5. Cooling and heating system.
6. Air blower (fan)

An air conditioning machine is shown in fig.

**Working :** A part of the air from air conditioned room is recirculated. The recirculated air is mixed with the fresh air in mixing chamber. There are filters in the mixing chamber which absorb dust from the mixed air. Now, the cleaned air is preheated by means of pipes in which hot water is passed. This function is performed by preheater in the mixing chamber. This is done because warmer air can absorb more water vapour.



**Fig.**

Also, in the mixing chamber, a part of air is cooled by the cooler system. The moisture content and temperature of the air emerging out from the cooler are adjusted to the desired values by adjusting the temperature of the cooler.

The air coming out from the cooler is mixed with the air coming straight from the preheater. Therefore, an air mixture of desired temperature and humidity is obtained. If the humidity is very low, then by means of spray-nozzles, water is added to air mixture. By doing so, the temperature is also decreased. To maintain the desired temperature, the air is again passed through a reheater. As a result, we get the air of desired temperature and humidity.

The air blower or fan behind the reheater forces the conditioned air through ducts into the room.

#### Q.6. Give the properties of substances at low temperatures.

**Ans :** At low temperatures, the matter exhibits some peculiar properties as compared to the properties shown at ordinary temperatures. At low temperatures and very low temperatures, followings are the few surprising and unexpected properties of the substances :

1. At temperatures below 90 K, most of the chemical reactions cease to take place. At these temperatures, animal and vegetable matter can be preserved without putrefaction.
2. Certain materials like cotton and wool exhibit the property of fluorescence when exposed to the temperature of liquid air for some time.
3. At temperatures below 83 K lead loses elasticity and attains a plastic state. The substances like rubber and glass become extremely brittle at these temperatures. Rubber cooled to such a low temperatures breaks into pieces just like a cork when hammered.
4. For all substances, the atomic heat (product of atomic weight and specific heat) tends to become zero as the absolute zero of temperature is reached.
5. Elements like oxygen are not paramagnetic in nature in their gaseous state. But, when they are converted into liquids at low temperatures, they become paramagnetic.
6. The magnetic susceptibility of certain paramagnetic salts like copper sulphate vary inversely at the absolute temperature in the region of low temperatures.



7. The entropy of a substance tends to zero value when it is exposed to very low temperature.
8. The electrical resistance of most metals decreases as the temperature is reduced. At a particular temperature, the resistance completely vanishes, i.e., the conductivity becomes infinity. Under this situation the ordinary conducting material becomes super-conductor (infinity conductivity). the temperature is called as transition temperature. It is found that the resistance of mercury vanishes suddenly at temperature of about 4.2 K. Good conductors like copper and platinum offer almost negligible resistance at temperature below 43 K.

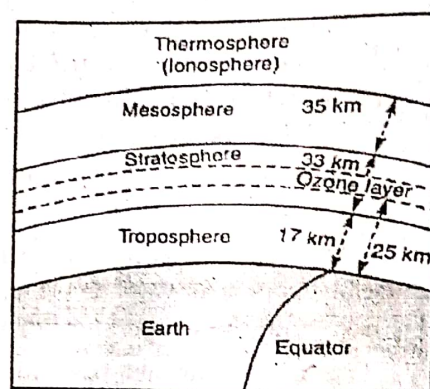
The property of a metal of completely losing its electrical resistance in the neighbourhood of absolute zero of temperature is called superconductivity.

9. Below 2.17 K, helium is called as He II and it exhibits super-fluidity. Its viscosity is very low and it can pass through a capillary tube without any resistance. The property is known as super-fluidity.

**Q.7. Explain the effects of chloro-fluoro carbons on ozone layer.**

**Ans :** In order to consider the effects of chloro and fluoro carbons on ozone layer, first of all, we consider the ozone layer and then ultraviolet (U.V.) radiations and their harmful effects.

1. **Ozone layer :** The gaseous envelope surrounding our earth is called the atmosphere. The atmosphere is composed of mass of air containing primarily gases as  $N_2$ ,  $O_2$ ,  $CO_2$ ,  $H_2$ ,  $O_3$ ,  $O_2$ ,  $O$ , etc. The atmosphere is mainly divided into four regions as shown in fig. The major regions of the atmosphere, their altitude ranges, temperature ranges and the main gases present in those regions are shown in table.



**Fig.**

**Table : Major regions of our atmosphere**

Region	Altitude range (in km)	Temperature range ( $^{\circ}C$ )	Major gases present
Troposphere	0-11	15 to $(-56)$	$N_2$ , $O_2$ , $H_2$ , $CO_2$ , $O_3$
Stratosphere	11-50	$-56$ to $-2$	$O_3$
Mesosphere	50-85	$-2$ to $-92$	$O_2$ , NO
Thermosphere (Ionosphere)	85-500	$-92$ and below it.	$O_2$ , O, NO

The layer of the atmosphere about 235 km from the earth's surface is known as ozone layer. The ozone ( $O_3$ ) molecules present in this layer absorb ultraviolet radiations from the sun to the atmosphere. The ozone molecules decompose into oxygen molecules ( $O_2$ ) and single oxygen atoms (O). in this way, the ozone layer acts as a protective shield surrounding our earth. So, the ozone layer protects us from direct exposure to U.V. radiations from the sun.

**U.V. radiations and their harmful effects :**

The U.V. radiations damage the deoxyribonucleic acid molecules (DNA). They have the following deleterious effects : i) They damage the DNA of reproductive molecules in all living beings. ii) They increase the occurrence of human skin cancer. iii) They increase the damage of human and plant life. iv) They reduce the rate and efficiency of photosynthesis. v) They affect the global climate, i.e., increase the global warming.

**Effect of chloro and fluoro carbons on ozone layer :**

The chloro-fluoro carbons are responsible for the destruction of ozone layer. Already about 5%

ozone layer has been depleted. (i.e., a hole has been formed in ozone layer) at global level. The depletion of ozone layer is greatest over the south pole where about 50% hole is formed in the ozone layer. The hole in the ozone layer results in increased U.V. radiations directly reaching the earth. These radiations produce harmful effects on human life, plant life and under water aquatic life also.

Therefore, chloro and fluoro carbons produce destruction of ozone layer which is harmful for human life because U.V. radiations reach the earth through destructed ozone layer.

### PROBLEMS

1. Calculate the change in temperature when carbon-di-oxide gas suffers Joule-Thomson expansion at  $27^\circ\text{C}$ . The pressures on the two sides of the porous wall are 50 atmospheres and one atmosphere. Given  $a = 0.363 \text{ nt-m}^4/\text{mol}^2$ ,  $b = 42.7 \times 10^{-6} \text{ m}^3/\text{mol}$ . and  $C_p = 8.75 \text{ cal}/(\text{mol-K})$ .

Sol. Given that  $P_1 - P_2 = 50 - 1 = 49 \text{ atm.} = 49 \times (1.01 \times 10^5) = 49.5 \times 10^5 \text{ nt/m}^2$   
 $JC_p = (4.18 \text{ joule/cal}) \times [8.75 \text{ cal}/(\text{mol-K})] = 36.6 \text{ joule}/(\text{mol-K})$

$$\frac{2a}{RT} = \frac{2 \times 0.363 \text{ nt-m}^4/\text{mol}^2}{8.31 \text{ joule}/(\text{mol-K}) \times 300 \text{ K}} = 291 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\left( \frac{2a}{RT} - b \right) = 29.1 \times 10^{-6} - 42.7 \times 10^{-6} = 248 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\Delta T = - \frac{(P_1 - P_2)}{JC_p} \times \left[ \frac{2a}{RT} - b \right] = - \frac{49.5 \times 10^5}{36.6} \times 248 \times 10^{-6} = -33.5 \text{ K} = -306.5^\circ\text{C}$$

2. Calculate the temperature of inversion in case of  $\text{H}_2$  and  $\text{CO}_2$  from the given data.  $T_c$  for  $\text{H}_2$  is  $-239.9^\circ\text{C}$  and for  $\text{CO}_2$  is  $31^\circ\text{C}$ .

Sol. Here,  $(T_c)_{\text{H}_2} = -239.9^\circ\text{C} = -239.9 + 273 = 33.1 \text{ K}$   
 and  $(T_c)_{\text{CO}_2} = 31^\circ\text{C} = 31 + 273 = 304 \text{ K}$

We know that  $T_i = \left( \frac{27}{4} \right) T_c$   $(T_i)_{\text{H}_2} = \left( \frac{27}{4} \right) \times 33.1 = 223.4 \text{ K} = -49.6^\circ\text{C}$

and  $(T_i)_{\text{CO}_2} = \frac{27}{4} \times 304 = 2052 \text{ K} = 1779^\circ\text{C}$

3. Calculate the temperature of inversion of helium gas.

Give :  $a = 3.44 \times 10^{-3} \text{ nt-m}^4/\text{mol}^2$  and  $b = 0.0237 \times 10^{-3} \text{ m}^3/\text{mol}$  and  $R = 8.31 \text{ joule}/(\text{mol-K})$ .

Sol. The temperature of inversion is given by

$$T_i = \frac{2a}{Rb} = \frac{2 \times 3.44 \times 10^{-3}}{8.31 \times 0.0237 \times 10^{-3}} = 35 \text{ K} = -238^\circ\text{C}$$

4. If critical temperature of a gas is  $16.6^\circ\text{C}$ , find its Boyle's temperature.

Sol.  $T_c = \frac{8}{27} T_B$  or  $T_B = \frac{27}{8} T_c$

$$T_B = \frac{27}{8} \times 289.6 \quad (\because T_c = 273 + 16.6^\circ\text{C} = 289.6 \text{ K})$$

or  $T_B = 977.4 \text{ K} = 704.4^\circ\text{C}$

—O—



## UNIT - V

# QUANTUM THEORY OF RADIATION

### LONG ANSWER QUESTIONS

**Q. 1. What is Planck's Hypothesis ? Derive Planck's formula for the distribution of energy in black body radiation. Show that Wien's and Rayleigh-Jeans laws are special cases of Planck's radiation laws.**

**Ans :** The classical theory of radiation, due to the assumption that energy changes of radiators take place continuously, could not explain the experimentally observed distribution of energy in the spectrum of a black body. Planck, therefore, was led to make an important hypothesis known as Planck's hypothesis. According to it, "A black body radiation chamber is filled up not only with radiation; but also with simple harmonic oscillators or resonators of the molecular dimensions, and the exchange of energy between matter and radiation does not take place continuously but discontinuously and discretely as an integral multiple of small unit of energy called the **quantum** or **photon**. The vibration of the resonator entails one degree of freedom only. Thus, if the equipartition principle of energy were applicable. The energy associated with each resonator would have been  $kT$  unit of energy with would be partly kinetic and partly potential.

Planck assumed that the energy of a photon is proportional to the frequency of radiation, i.e.,  $\epsilon = h\nu$ .

Where  $h$  is a universal constant called the "Planck's constant".

This means that an oscillator of frequency  $\nu$  can only emit or absorb the radiation in units of quanta of magnitude  $h\nu$ . The emission of radiation corresponds to a decrease and absorption to an increase in energy and amplitude of an oscillator, which would be partly kinetic and partly potential. Thus  $\epsilon = nh\nu$ ,  $n = 0, 1, 2, 3, \dots$

The hypothesis was originally made to explain the experimentally observed spectrum of black-body radiation. Later it was used by Einstein to explain the photoelectric effect and the variations in specific heats of solids and gases. Bohr used it to explain atomic spectra. It has also been used to explain photochemical reactions.

**A) Planck's radiation Law :** If  $N$  is the total number of Planck's resonators and  $E$  their total energy, then average energy per Planck oscillator is given by

$$\bar{\epsilon} = \frac{E}{N} \quad \dots (1)$$

According to Maxwell's law of molecular motion if  $\epsilon$  is a certain amount of energy, the probabilities that a system will have energies.

$0, \epsilon, 2\epsilon, \dots, r\epsilon, \dots$  are in the ratio.

$$1 : e^{-\frac{\epsilon}{kT}} : e^{-\frac{2\epsilon}{kT}} : e^{-\frac{r\epsilon}{kT}} : \dots \text{ etc.}$$

If  $N_0$  is the number of resonators having energy zero, then the number of resonators  $N_1$  having energy  $\epsilon$  will be  $N_0 e^{-\frac{\epsilon}{kT}}$ , the number of resonators  $N_2$  having energy  $2\epsilon$  will be  $N_0 e^{-\frac{2\epsilon}{kT}}$  and in general, the number of resonators  $N_r$  having energy  $r\epsilon$  will be  $N_0 e^{-\frac{r\epsilon}{kT}}$  and so on.

$$\therefore N = N_0 + N_1 + N_2 + \dots + N_r + \dots$$

$$= N_0 + N_0 e^{-\frac{\epsilon}{kT}} + N_0 e^{-\frac{2\epsilon}{kT}} + \dots + N_r e^{-\frac{r\epsilon}{kT}} + \dots = N_0 \left[ 1 + e^{-\frac{\epsilon}{kT}} + e^{-\frac{2\epsilon}{kT}} + \dots + e^{-\frac{r\epsilon}{kT}} + \dots \right]$$

Putting  $e^{-\frac{h\nu}{kT}} = y$  ..... (2)

$$\therefore N = N_0 [1 + y + y^2 + \dots + y^r + \dots]$$

or  $N = \frac{N_0}{(1-y)}$  ..... (3)

The total energy of Planck's resonators will be

$$E = 0 \times N_0 + \epsilon \times N_1 + 2\epsilon \times N_2 + \dots + r\epsilon \times N_r + \dots$$

$$= 0 \times \epsilon N_0 e^{-\frac{h\nu}{kT}} + 2\epsilon N_0 e^{-\frac{2h\nu}{kT}} + \dots + r\epsilon N_0 e^{-\frac{rh\nu}{kT}} + \dots = N_0 \epsilon \left[ e^{-\frac{h\nu}{kT}} + 2e^{-\frac{2h\nu}{kT}} + \dots + re^{-\frac{rh\nu}{kT}} \right]$$

$$N_0 = \frac{N_0}{(1-y)^2} \quad \dots \dots \dots (4)$$

Therefore the average energy of resonator will be

$$\bar{\epsilon} = \frac{E}{N} = \frac{N_0 \epsilon \frac{y}{(1-y)^2}}{\frac{N_0}{1-y}} = \frac{\epsilon y}{1-y} = \frac{\epsilon e^{-\frac{h\nu}{kT}}}{1-e^{-\frac{h\nu}{kT}}} \quad \text{(or)} \quad \bar{\epsilon} = \frac{\epsilon}{e^{\frac{h\nu}{kT}} - 1} \quad \dots \dots \dots (5)$$

According to Planck's hypothesis of quantum theory  $\epsilon = h\nu$ , therefore the average energy of Planck's oscillator is given by

$$\bar{\epsilon} = \frac{\epsilon}{e^{\frac{h\nu}{kT}} - 1} \quad \dots \dots \dots (6)$$

Now the energy density belonging to the range  $d\nu$  can be obtained by multiplying the average energy of Planck's oscillator by the number of oscillators per unit volume, in the frequency range  $\nu$  and  $\nu + d\nu$ , i.e.

$$\text{or} \quad E_\nu d\nu = \left( \frac{8\pi\nu^2}{c^3} d\nu \right) \left( \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \right) \quad \text{or} \quad E_\nu d\nu = \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{e^{\frac{h\nu}{kT}} - 1} d\nu \quad \dots \dots \dots (7)$$

where  $E_\nu d\nu$  is energy density (i.e., total energy per unit volume) belonging to the range  $d\nu$ .

Eqn. (7) is called "Planck's radiation law".

The energy density  $E_\lambda d\lambda$  belonging to range  $d\lambda$  can be obtained by using the relation  $\nu = (c/\lambda)$  and hence  $|d\nu| = |(c/\lambda^2)d\lambda|$ , we get

$$E_\lambda d\lambda = \frac{8\pi h}{c^3} \left( \frac{c^3}{\lambda^3} \right) \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \left( -\frac{c^3}{\lambda^3} d\lambda \right) = \frac{8\lambda hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} d\lambda \quad \dots \dots \dots (8)$$

This is Planck's radiation law in terms of wavelength.

**b) Deduction of Wien's formula from Planck's Radiation formula :** We know Planck's Radiation formula is,

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \left[ \exp\left(\frac{hc}{\lambda kT}\right) - 1 \right]^{-1} d\lambda \quad \dots \dots \dots (1)$$



For small temperatures,  $\exp\left(\frac{-hc}{\lambda kT}\right) \gg 1$  and "1" can be neglected in the denominator of the above equation

$$\therefore E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \exp\left(\frac{-hc}{\lambda kT}\right) d\lambda \quad \dots\dots (2)$$

Taking  $8\pi hc = a$ ;  $\frac{hc}{k} = b$ , we can write  $E_{\lambda} d\lambda = \frac{a}{\lambda^5} e^{\frac{-b}{\lambda T}} d\lambda \quad \dots\dots (3)$

This is Wien's formula which agrees at short wavelengths.

**c) Deduction of Rayleigh-Jeans formula from Planck's formula :**

For large temperatures  $\exp\left(\frac{hc}{\lambda kT}\right) = 1 + \frac{hc}{\lambda kT} \quad \dots\dots (4)$

We know Planck's formula,

$$\therefore E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{\exp\left(\frac{hc}{\lambda kT}\right) - 1} \quad \therefore E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{\left(1 + \frac{hc}{\lambda kT}\right) - 1}$$

$$\therefore E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{\frac{hc}{\lambda kT}} \quad \therefore E_{\lambda} d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

$\dots\dots (5)$

**d) Deduction of Wiens Displacement Law from Planck's formula :** We know Planck's formula is

$$E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{\frac{hc}{\lambda kT}} - 1}$$

$$\left(\frac{\partial E_{\lambda}}{\partial \lambda}\right) = \frac{-5(\partial \pi hc)}{\lambda^6} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} + \frac{8\pi hc}{\lambda^5} \times \frac{\frac{hc}{\lambda^2 kT} \cdot e^{\frac{hc}{\lambda kT}}}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)^2}$$

$$= \frac{-40\pi hc}{\lambda^6} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} + \frac{8\pi hc}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \frac{e^{\frac{hc}{\lambda kT}}}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)^2} \quad \dots\dots (6)$$

For maximum value of  $E_{\lambda}$ ,  $\frac{\partial E_{\lambda}}{\partial \lambda} = 0$

$$\therefore \frac{-40\pi hc}{\lambda^6} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} + \frac{8\pi hc}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \frac{e^{\frac{hc}{\lambda kT}}}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)^2} = 0$$

$$\therefore \left( \frac{8\pi hc}{e^{\frac{hc}{\lambda kT}} - 1} \right) \lambda^6 \times \left( -5 + \frac{Pe^p}{e^p - 1} \cdot \frac{e^{\frac{hc}{\lambda kT}}}{\left( e^{\frac{hc}{\lambda kT}} - 1 \right)} \right) = 0 \quad -5 + \frac{hc}{\lambda kT} \cdot \frac{e^{\frac{hc}{\lambda kT}}}{\left( e^{\frac{hc}{\lambda kT}} - 1 \right)} = 0$$

Put  $\frac{hc}{\lambda kT} = P$  in the above,  $-5 + \frac{Pe^p}{e^p - 1} = 0 \quad \therefore \frac{Pe^p}{e^p - 1} = 5$

From mathematical principle,  $P = 4.965$

$$\therefore \frac{hc}{\lambda kT} = 4.965$$

$$\therefore \lambda T = \frac{hc}{4.965k} = \text{constant}$$

$$\therefore \lambda T = \text{constant}$$

$$\therefore \lambda \propto \frac{1}{T}$$

This is Wiens-displacement law.

**Q. 2. What is Black Body ? Discuss the spectral energy distribution of black body radiation?**

**Ans :** Black body is that which absorbs all the incident radiation and does not reflect the rays incident on it. The absorbing power of the black body is about 100% and the emissive power is also about 100% but the reflecting power is almost zero. Hence the black body appears dark when it is cold and bright when it is hot.

**Black body radiation :** A perfectly black body is one which absorbs completely radiations of all wavelengths incidenting on it. For all practical purposes a lampblackend surface may be treated as a perfectly black body. A perfectly black body is a good absorber as well as a good radiator. So if it is heated to a suitable high temperature, it emits radiations of all wavelengths. Hence such a radiation is often spoken as black body radiation (or full radiation or total radiation).

**Ferry's Black Body :** Ferry's black body consists of two hollow concentric spheres  $S_1$ ,  $S_2$  provide with a narrow opening A and the projection B opposite to A. The inside surface of  $S_2$  is coated with lamp black and the outside surface of  $S_1$  is brightly polished. The space between  $S_1$ ,  $S_2$  is completely evacuated. The incident radiation through A suffers a number of reflections inside the sphere  $S_2$  and it is absorbed in it. The projection B avoids the reflection of radiation incidenting normally on the surface  $S_2$ . The narrow opening acts as black body absorbing all the incident radiation when the body is cold and emitting radiation of all wavelengths when it is hot.

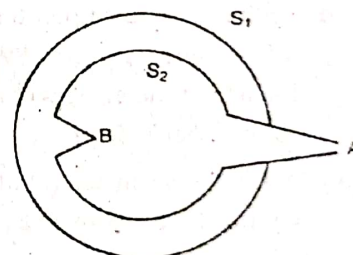


Fig.

**Wien's Black Body :** The Wien's black body consists of a cylindrical hollow metallic chamber C. The thin platinum foil is wound over it. The chamber C can be heated by passing electric current through the platinum foil. The inner surface of the chamber is made black. The temperature of the chamber is measured by the thermocouple thermometer. The radiation from the chamber is limited by a number of blackened diaphragms D and finally emerges out of H. The chamber is protected by the co-axial porcelain tubes P. P with air space between them.

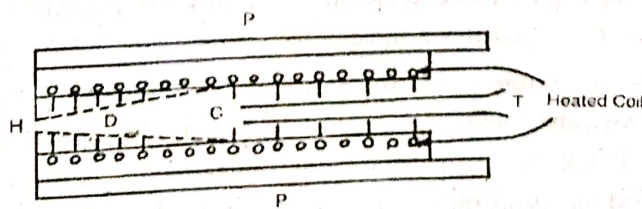


Fig.



### Spectral Distribution in Black Body

**Radiation :** Lummer and Pringsheim investigated the distribution of energy among the radiation emitted by a black body at different temperatures.

The experimental arrangement of Lummer and Pringsheim is shown in Fig. The black body was a small aperture in an electrically heated chamber whose temperature was recorded by a thermocouple.

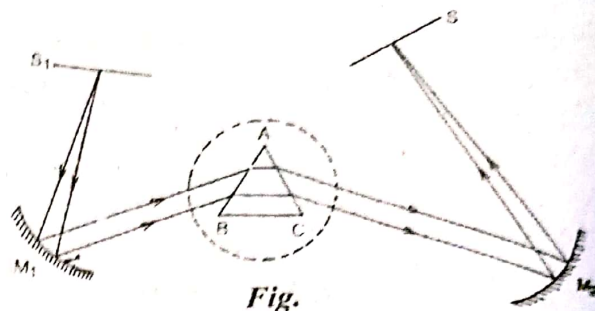


Fig.

The radiations from the black body pass through the slit  $S_1$  and fall on the reflector  $M_1$ . After being reflected, the parallel beam of radiation falls on a rock-salt or fluorspar prism  $ABC$  placed on the turn table of the spectrometer. The emergent light is focussed by the reflector (concave mirror)  $M_2$  on a line bolometer placed behind the slit  $S_2$ . The bolometer is connected to a sensitive galvanometer. The turn table is rotated slowly so that different parts of the radiation spectrum successively fall on the bolometer circuit and are read. The intensity of each line is proportional to the deflection in the galvanometer. Then a curve is drawn between intensity and the wavelength. Then the body is heated to different temperatures and the curves are drawn for various temperatures.

#### Result, from the curves :

- The energy is not uniformly distributed in the radiation spectrum of a black body.
- At a given temperature, the intensity of radiations increases with increase of wavelength and becomes maximum at a particular wavelength. By further increasing the wavelength, intensity of heat radiations decreases.
- An increase in temperature causes a decrease in  $\lambda$  such that  $\lambda T = \text{constant} = 0.02896 \text{ cm K}$ , where  $\lambda$  is the wavelength for which the energy emitted is maximum. This relation is called Wien's displacement law.
- An increase in temperature causes an increase in energy emitted by the body at a particular temperature for the range of the wavelengths considered. This area increases with increase of temperature. It is found that area is directly proportional to the fourth power of absolute temperature i.e.,  $E \propto T^4$  which is Stefan's Law.

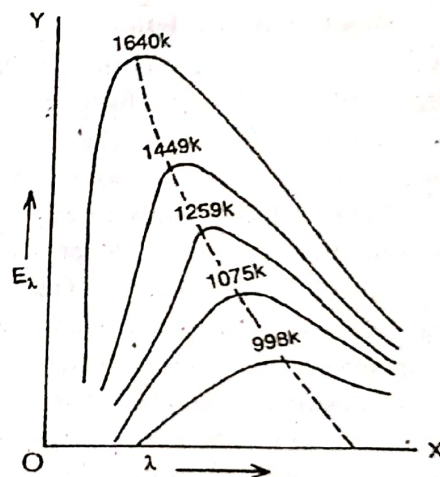


Fig.

**Q. 3. Define Solar Constant. Explain how it is determined using Angstrom's Pyroheliometer. Using it estimate the surface temperature of sun.**

**Ans : Solar Radiation :** The sun emits radiation continuously in space. A very small part of solar radiation reaches the earth. But of this incoming radiation a considerable portion is lost by reflection and scattering by the earth's atmosphere. The best reflecting constituents of the atmosphere are water vapour, snow and cloud. The scattering is partly due to the dust particles and due to the air molecules. Further, the radiation is absorbed heavily by the earth's atmosphere.

#### Experiment to Determine the solar constant :

**Definition of solar constant :** Solar constant is the rate at which the solar radiation is received by one square centimeter of a black surface held at right angles to the sun's rays and placed at the mean distance of the earth provided the atmosphere were not present. The value of solar constant is  $1.937 \text{ cal-cm}^{-2} \text{ min}^{-1}$ .



**Experiment :** Solar constant is determined by using the Angstrom's Pyroheliometer. It consists of two thin identical strips  $A$  and  $B$  of platinum or manganin. They are suitably mounted such that  $A$  is exposed to solar radiation falling normally on it and  $B$  is electrically heated and is shielded by the screen  $S$ .

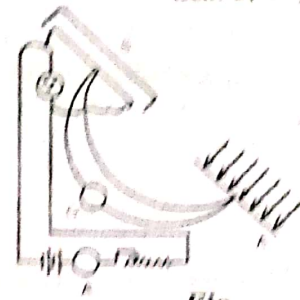


Fig.

When the strip  $A$  is exposed to solar radiation it receives heat and the deflection will be produced in the galvanometer. The current is passed through the strip  $B$  and the strength of the current is adjusted until the galvanometer does not show any deflection. In this case the rate at which the strip  $A$  receives solar radiation and rate at which heat is generated in  $B$  are equal.

If  $\alpha$  is the area of the strip  $A$ , the solar radiation received per minute per square centimetre per min

$$\text{is } \frac{EI \times 60}{\alpha \times 4.2}$$

$$\text{That is } S = \frac{EI \times 60}{\alpha \times 4.2} \text{ cal. cm}^{-2} \cdot \text{min}^{-1}.$$

( $E$  = voltmeter reading in volts,  $I$  = ammeter reading in amperes and  $\alpha$  = area of the strip  $A$  in square centimetres).

The experiment is repeated at different times of the day and the solar constant  $S$  is observed and the Zenith distance  $Z$  of the sun or angular elevation  $Z$  of the sun is noted. If  $S_0$  is the true solar constant it can be shown that  $S = S_0 a^{\sec Z}$  where  $a$  is the transmission coefficient which varies from 0.55 to 0.85. Taking logarithms  $\log S = \log S_0 + \sec Z \log(a)$ . Draw the graph taking  $\log S$  along X-axis and  $\sec Z$  along Y-axis. The intercept on Y-axis gives  $\log S_0$  from which  $S_0$  can be calculated. The value of  $S_0$  will be found to be equal to  $1.94 \text{ cal-cm}^{-2}\cdot\text{min}^{-1}$ .

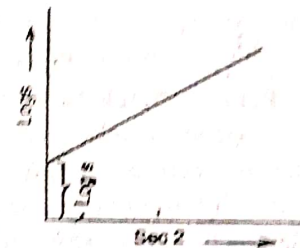


Fig.

**c) Temperature of the sun :** The physical divisions of the sun are i) the Central Hot core terminating in a surface called the photosphere ii) the Reversing Layer, which is supposed to contain most of the terrestrial elements in vapour form and gives rise to the Fraunhofer lines in the solar spectrum iii) the Chromosphere which is the extension of the reversing layer and the chromosphere can be seen only during total solar eclips and iv) the Corona.

The sun is a huge mass of gas (mass :  $2 \times 10^{34} \text{ gm}$ ) held together by the gravitational force of attraction amongst the atoms. The temperature at the centre of the sun will be about  $10^6 \text{ K}$ . The temperature of the sun has a vague meaning. We assume that the term photosphere is the limiting surface and we can measure the temperature of the photosphere and this measured temperature is referred to the black body temperature of the sun.

Let  $E$  be the amount of radiation emitted per second by one square centimetre of the sun's surface. If ' $a$ ' be the radius of the sun, the total amount of energy radiated by the sun in one minute =  $4\pi a^2 \times R \times 60$ .

This energy is received by a sphere which is equal to the earth's orbit.

If  $b$  is the radius of the earth's orbit,  $S_0$  is the solar constant the total energy of radiation received by the sphere of radius  $b$  is  $4\pi b^2 S_0$ .

$$\therefore 4\pi a^2 \times R \times 60 = 4\pi b^2 S_0$$

$$\therefore R = \left(\frac{b}{a}\right)^2 \times \frac{S_0}{60} \quad \dots\dots (1)$$

$$\text{From Stefan's law } E = \sigma T^4 \quad \dots\dots (2)$$



Hence from (1) and (2),  $\sigma T^4 = \left(\frac{b}{a}\right)^4 \times \frac{S_0}{60}$

$$T = \left(\frac{b^4 S_0}{a^4 60 \sigma}\right)^{1/4}$$

The black body temperature  $T$  of the sun can be calculated. This calculated temperature is less than the temperature of the sun.

### SHORT ANSWER QUESTIONS

**Q. 1. Define black body? Explain Ferry's Black body and Wien's black body with neat sketch?**

**Ans :** Black body is that which absorbs all the incident radiation and does not reflect the rays incident on it. The absorbing power of the black body is about 100% and the emissive power is also about 100% but the reflecting power is almost zero. Hence the black body appears dark when it is cold and bright when it is hot.

**Black body radiation :** A perfectly black body is one which absorbs completely radiations of all wavelengths incidenting on it. For all practical purposes a lampblackend surface may be treated as a perfectly black body.

A perfectly black body is a good absorber as well as a good radiator. So if it is heated to a suitable high temperature, it emits radiations of all wavelengths. Hence such a radiation is often spoken as black body radiation (or full radiation or total radiation).

**Ferry's Black Body :** Ferry's black body consists of two hollow concentric spheres  $S_1$ ,  $S_2$  provide with a narrow opening  $A$  and the projection  $B$  opposite to  $A$ . The inside surface of  $S_2$  is coated with lamp black and the outside surface of  $S_1$  is brightly polished. The space between  $S_1$ ,  $S_2$  is completely evacuated. The incident radiation through  $A$  suffers a number of reflections inside the sphere  $S_2$  and it is absorbed in it. The projection  $B$  avoids the reflection of radiation incidenting normally on the surface  $S_2$ . The narrow opening acts as black body absorbing all the incident radiation when the body is cold and emitting radiation of all wavelengths when it is hot.

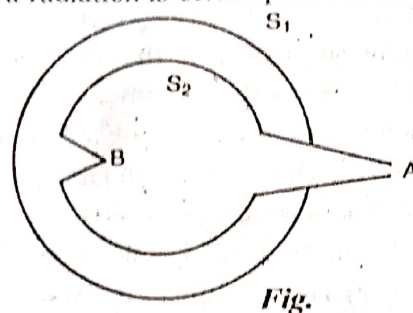


Fig.

**Wien's Black Body :** The Wien's black body consists of a cylindrical hollow metallic chamber  $C$ . The thin platinum foil is wound over it. The chamber  $C$  can be heated by passing electric current through the platinum foil. The inner surface of the chamber is made black. The temperature of the chamber is measured by the thermocouple thermometer.

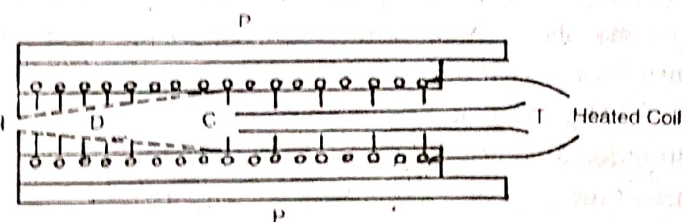


Fig.

The radiation from the chamber is limited by a number of blackened diaphragms  $D$  and finally emerges out of  $H$ . The chamber is protected by the co-axial porcelain tubes  $P$ ,  $P$  with air space between them.

**Q. 2. Define the laws of thermal radiation.**

**Ans : 1. Kirchhoff's Law :** This law states that at a given temperature, the ratio of emissive power to the absorptive power for given wavelength is the same for all bodies and is equal to the emissive power of a black body at the same temperature.

Consider the case of a body (with any type of surface), at equilibrium in an enclosure of uniform temperature. Let the energy  $dQ_\lambda$  (within wavelength range  $\lambda$  and  $\lambda + d\lambda$ ) which depends only upon the temperature, be incident on the unit area of the body per second. Now,

Energy absorbed by the body = energy emitted by the body

$$a_{\lambda} dQ_{\lambda} = e_{\lambda} d\lambda$$

where  $a_{\lambda}$  is the absorptive power and  $e_{\lambda}$  is emissive power of the body. Hence,

$$\frac{e_{\lambda}}{a_{\lambda}} = \frac{dQ_{\lambda}}{d\lambda} = \text{constant.}$$

( $\odot$ )  $\frac{dQ_{\lambda}}{d\lambda}$  depends only on temperature and for a given temperature it is constant)

This is known as Kirchhoff's law.

**2. Stefan-Boltzmann Law :** This law states that the total amount of radiant energy emitted by a black body per second per unit area is directly proportional to the fourth power of its absolute temperature. i.e.,

$$E \propto T^4 \text{ or } E = \sigma T^4$$

where  $\sigma$  is called as Stefan's constant. It has a value  $5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ . This law is strictly true only when the medium surrounding the black body is vacuum. Stefan established this law experimentally in 1879. The same law was established in 1884 by Boltzmann theoretically from thermodynamical considerations. Hence, this law sometimes is known as Stefan-Boltzmann law.

Now consider the case of a black body  $B_1$  at absolute temperature  $T_1$  which is surrounded by another black body  $B_2$  at absolute temperature  $T_2$ . Now,

$$\text{Heat lost by black body } B_1 = \sigma T_1^4$$

$$\text{Amount of heat absorbed by black body A from black body } B_2 = \sigma T_2^4$$

$\therefore$  Net amount of heat emitted by body  $B_1$  per sec per unit area

$$\left( \frac{dQ}{dt} \right) = \sigma (T_1^4 - T_2^4),$$

This is the form of Stefan-Boltzmann law.

**3. Wien's Law :** In 1896, while investigating the energy distribution over different wavelengths. Wien showed that the maximum energy point shifts towards the shorter wavelengths side when the temperature of the body is raised. He showed that

$$\lambda_m T = \text{constant}$$

where  $\lambda_m$  is the wavelength corresponding to maximum energy emission from a black body at absolute temperature  $T$ . He also showed that the maximum energy emitted by a black body is proportional to the fifth power of its absolute temperature. Hence,

$$(E_{\lambda})_{\max} \propto T^5 \quad \text{or} \quad (E_{\lambda})_{\max} / T^5 = \text{constant.}$$

This is called as Wien's displacement law.

Wien by applying Maxwell's law for distribution of velocities and the principle of equipartition of kinetic energy gave the expression for  $E_{\lambda}$  as

$$E_{\lambda} = C_1 \lambda^{-5} e^{-C_2/\lambda T}.$$

where  $C_1$  and  $C_2$  are constants.

**4. Rayleigh-Jean's Law :** According to Rayleigh-Jean's law, the energy distribution in the thermal spectrum is given by

$$E_{\lambda} = \frac{8\pi kT}{\lambda^4},$$



where  $k$  is Boltzmann constant.

**5. Planck's Law :** On the basis of quantum theory, Planck derived the following formula for the energy distribution in thermal spectrum

$$E_{\lambda} = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

where  $h$  is Planck's constant,  $c$ , the velocity of light and  $k$  being the Boltzmann constant.

It should be remembered that Wien's formula agrees for short wavelengths region while Rayleigh-Jeans formula agrees for long wavelengths region. Planck's formula covers the entire range.

**Q. 3. Explain the construction and working of ANGSTROM's pyrhelio meter.**

**Ans :** Experiment to Determine the solar constant :

**Definition of solar constant :** Solar constant is the rate at which the solar radiation is received by one square centimeter of a black surface held at right angles to the sun's rays and placed at the mean distance of the earth provided the atmosphere were not present. The value of solar constant is  $1.937 \text{ cal-cm}^{-2} \text{ min}^{-1}$ .

**Experiment :** Solar constant is determined by using the Angstrom's Pyroheliometer. It consists of two thin identical strips  $A$  and  $B$  of platinum or manganin. They are suitably mounted such that  $A$  is exposed to solar radiation falling normally on it and  $B$  is electrically heated and is shielded by the screen  $S$ .

When the strip  $A$  is exposed to solar radiation it receives heat and the deflection will be produced in the galvanometer. The current is passed through the strip  $B$  and the strength of the current is adjusted until the galvanometer does not show any deflection. In this case the rate at which the strip  $A$  receives solar radiation and rate at which heat is generated in  $B$  are equal.

If  $\alpha$  is the area of the strip  $A$ , the solar radiation received per minute per square centimetre per min is  $\frac{EI \times 60}{\alpha \times 4.2}$

$$\text{That is } S = \frac{EI \times 60}{\alpha \times 4.2} \text{ cal. cm}^{-2} - \text{min}^{-1}.$$

( $E$  = voltmeter reading in volts,  $I$  = ammeter reading in amperes and  $\alpha$  = area of the strip  $A$  in square centimetres).

The experiment is repeated at different times of the day and the solar constant  $S$  is observed and the Zenith distance  $Z$  of the sun or angular elevation  $Z$  of the sun is noted. If  $S_0$  is the true solar constant it can be shown that  $S = S_0 \alpha^{\sec Z}$  where  $\alpha$  is the transmission coefficient which varies from 0.55 to 0.85. Taking logarithms  $\log S = \log S_0 + \sec Z \log (\alpha)$ . Draw the graph taking  $\log S$  along X-axis and  $\sec Z$  along Y-axis. The intercept on Y-axis gives  $\log S_0$  from which  $S_0$  can be calculated. The value of  $S_0$  will be found to be equal to  $1.94 \text{ cal-cm}^{-2} - \text{min}^{-1}$ .

**Q. 4. Write a short note on solar constant.**

**Ans :** The sun is radiating energy in all directions by virtue of its temperature. The earth receives only a fraction of this energy. A considerable portion of the incoming radiation is lost by reflection and scattering by terrestrial atmosphere. Moreover, the radiation is heavily absorbed by earth's atmosphere.

The absorption of radiation depends upon the time of day and the season of the year. Thus, the

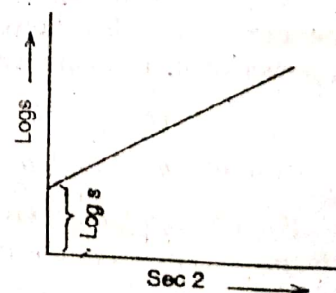
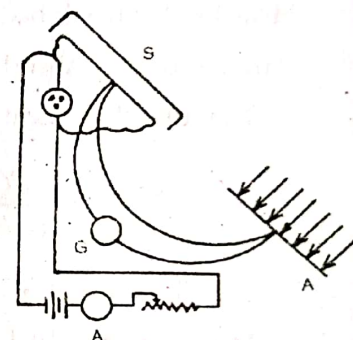


Fig.

amount of solar radiation received by the surface of the earth depends on the location, the time of the day, the time of the year, the weather and the tilt of the surface to sun rays.

Thus, we need a more constant quantity which is furnished by the rate at which solar radiations are received per unit area of a black surface held at right angles to the rays of the sun and placed at the mean distance of the earth. The constant quantity is termed as solar constant.

Solar constant is defined as the rate at which solar energy is received by a black surface per unit area placed normal to the sun rays at the mean distance of the earth from the sun in the absence of earth's atmosphere. Its value is  $1340 \text{ W m}^{-2}$  ( $1.92 \text{ cal cm}^{-2} \text{ min}^{-1}$ ).

**Q. 5. Derive Wein's law from Planck's radiation law.**

**Ans : Deduction of Wien's formula from Planck's Radiation formula :** We know Planck's Radiation formula is,

$$E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \left[ \exp\left(\frac{hc}{\lambda kT}\right) - 1 \right]^{-1} d\lambda \quad \text{..... (1)}$$

For small temperatures,  $\exp\left(\frac{hc}{\lambda kT}\right) \gg 1$  and "1" can be neglected in the denominator of the above equation

$$\therefore E_{\lambda} d\lambda = \frac{8\pi hc}{\lambda^5} \exp\left(\frac{-hc}{\lambda kT}\right) d\lambda \quad \text{..... (2)}$$

Taking  $\frac{hc}{\lambda kT} = a$ ,  $\frac{hc}{k} = b$ , we can write

$$E_{\lambda} d\lambda = \frac{a}{\lambda^5} e^{-\frac{b}{\lambda kT}} d\lambda \quad \text{..... (3)}$$

This is Wien's formula which agrees at short wavelengths.

**Q. 6. Derive Rayleigh-Tejan's law from Planck's radiation law.**

**Ans : Deduction of Wiens Displacement Law from Planck's formula :** We know Planck's formula is

$$\begin{aligned} E_{\lambda} d\lambda &= \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{e^{\frac{hc}{\lambda kT}} - 1} \\ \left(\frac{\partial E_{\lambda}}{\partial \lambda}\right) &= \frac{-5(\partial \pi hc)}{\lambda^6} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} + \frac{8\pi hc}{\lambda^5} \times \frac{\frac{hc}{\lambda^2 kT} \cdot e^{\frac{hc}{\lambda kT}}}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)^2} \\ &= \frac{-40\pi hc}{\lambda^6} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} + \frac{8\pi hc}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \cdot \frac{e^{\frac{hc}{\lambda kT}}}{\left(e^{\frac{hc}{\lambda kT}} - 1\right)^2} \quad \text{..... (6)} \end{aligned}$$



For maximum value of  $E_\lambda$ ,  $\frac{\partial E_\lambda}{\partial \lambda} = 0$

$$\therefore \frac{-40\pi hc}{\lambda^6} \cdot \frac{1}{e^{\frac{hc}{\lambda kT}} - 1} + \frac{8\pi hc}{\lambda^5} \times \frac{hc}{\lambda^2 kT} \left( \frac{e^{\frac{hc}{\lambda kT}}}{e^{\frac{hc}{\lambda kT}} - 1} \right)^2 = 0$$

$$\therefore \left( \frac{e^{\frac{hc}{\lambda kT}}}{e^{\frac{hc}{\lambda kT}} - 1} \right) \lambda^6 \times \left( -5 + \frac{Pe^p}{e^p - 1} \cdot \frac{e^{\frac{hc}{\lambda kT}}}{e^{\frac{hc}{\lambda kT}} - 1} \right) = 0 \therefore -5 + \frac{hc}{\lambda kT} \cdot \frac{e^{\frac{hc}{\lambda kT}}}{e^{\frac{hc}{\lambda kT}} - 1} = 0$$

Put  $\frac{hc}{\lambda kT} = P$  in the above,  $-5 + \frac{Pe^p}{e^p - 1} = 0$

$$\therefore \frac{Pe^p}{e^p - 1} = 5$$

From mathematical principle,  $P = 4.965$

$$\therefore \frac{hc}{\lambda kT} = 4.965 \quad \therefore \lambda T = \frac{hc}{4.965k} = \text{constant}$$

$$\therefore \lambda T = \text{constant} \quad \therefore \lambda \alpha = \frac{1}{T}$$

This is Wiens-displacement law.

### PROBLEMS

1. Calculate the surface temperature of the sun and moon given that  $\lambda_m = 4753$  and  $14\mu$  respectively,  $\lambda_m$  being wavelength of maximum intensity of emission.

Sol. According to Wien's displacement law

$$\lambda_m T = \text{constant} = 0.2898 \times 10^{-2} \text{ mK} \quad \text{or} \quad T = \frac{0.2898 \times 10^{-2}}{\lambda_m}$$

i) For sun,  $\lambda_m = 4753 \text{ \AA} = 4753 \times 10^{-10} \text{ m} \quad \therefore T_s = \frac{0.2898 \times 10^{-2}}{4753 \times 10^{-10}} = 6097 \text{ K}$

ii) For moon,  $T_m = \frac{0.2898 \times 10^{-2}}{14 \times 10^{-6}} \text{ (}\odot \text{ } 1\mu = 1 \text{ micron} = 10^{-6} \text{ m)} = 207 \text{ K}$

2. A black body radiator at  $0^\circ\text{C}$  radiates energy of  $3.2 \times 10^2 \text{ Jm}^{-2} \text{ sec}^{-1}$ . Deduce i) the value of stefan's constant, ii) the amount of heat radiated per second by a sphere of radius  $4 \text{ cm}$ , at a temperature  $1000^\circ\text{C}$  (Assumed to be a black body).

Sol. i) According to Stefan's law

$$E = \sigma T^4$$

Here  $E = 3.2 \times 10^2 \text{ Jm}^{-2} \text{ sec}^{-1}$  and  $T = 0^\circ\text{C} = 273 \text{ K}$

$$\therefore \sigma = \frac{E}{T^4} = \frac{3.2 \times 10^2}{(273)^4} = 5.7 \times 10^{-8} \text{ Jm}^{-2} \text{ sec}^{-1} \text{ K}^{-4}$$

- ii) The amount of energy radiated per second by a sphere of radius 4cm at temperature  $1000^{\circ}\text{C}$  ( $1273^{\circ}\text{K}$ ) is given by

$$= \sigma T^4 \times \text{area of surface} = \sigma T^4 \times 4\pi r^2$$

$$= (5.7 \times 10^{-8}) (1273)^4 \times 4 \times 3.14 \times (0.04)^2 = 1.2 \times 10^3 \text{ J/s.}$$

3. A black body at  $500^{\circ}\text{C}$  has a surface area of  $0.5\text{m}^2$  and radiate heat at the rate of  $1.02 \times 10^4 \text{ Js}^{-1}$ . Calculate the Stefan's constant.

Sol. The total heat radiated per second by a black body is given by  $E = \sigma T^4 \times A$   
where  $A$  is the surface area and  $T$  is absolute temperature of the body.

$$\therefore \sigma = \frac{E}{T^4} \quad \text{Substituting the given values, we get}$$

$$\therefore \sigma = \frac{1.02 \times 10^4}{0.5 \times (773)^4} = 5.7 \times 10^{-8} \text{ Joule}/(\text{m}^2 \cdot \text{sec} \cdot \text{K}^4)$$

4. What is the wavelength of the maximum intensity radiation, radiated from a source having temperature  $3000 \text{ K}$ . The Wien's constant is  $0.29 \text{ cm.K}$ .

Sol. According to Wien's law  $\lambda_m T = b$

$$\therefore \lambda_m = \frac{b}{T} = \frac{0.29 \text{ cm.K}}{3000 \text{ K}} = 9666 \times 10^{-8} \text{ cm} = 9666 \text{ }^{\circ}\text{A}$$

5. If  $\lambda_m$  for solar radiation is  $4753 \text{ }^{\circ}\text{A}$  and Wien's constant  $= 2.89 \times 10^{-3}$ , metre-K calculate the temperature of the photosphere.

Sol. According to Wien's law  $\lambda_m T = b$

$$\therefore T = \frac{b}{\lambda_m} = \frac{2.89 \times 10^{-3} \text{ metre-K}}{4753 \times 10^{-3} \text{ metre}}$$

6. A black body at  $1127^{\circ}\text{C}$  radiates maximum wavelength of 2 microns, if the wavelength of maximum energy of moon is 14 microns, what is the temperature of the moon?

Sol. Given that  $T_1 = 1127 + 273 = 1400^{\circ}\text{K}$   $\lambda_1 = 2\text{m}; \lambda_2 = 14\text{m}; T_2 = ?$

$$\therefore T_2 = \frac{\lambda_1 T_1}{\lambda_2} = \frac{1400 \times 2}{14} = 200^{\circ}\text{K}$$

Temperature of the moon  $T_2 = 200^{\circ}\text{K}$

7. Determine the temperature of the sun with help of Wien's displacement law, given

$b = 2.92 \times 10^{-3} \text{ mK}$ , maximum wavelength  $= 4900 \text{ }^{\circ}\text{A}$ .

Sol. Given that  $\lambda = 4900 \text{ AU}$ ;  $b = 2.92 \times 10^{-3}$

From Wien's displacement law  $\lambda_m T = b$

$$\therefore T = \frac{b}{\lambda_m} = \frac{2.92 \times 10^{-3}}{4900 \times 10^{-10}} = 5959^{\circ}\text{K}$$

Temperature of the sun,  $T = 5959^{\circ}\text{K}$



8. Calculate at what temperature a body would appear red and blue. The Wien's constant

$b = 3 \times 10^{-3} \text{ mK}$ . The maximum wavelength of emission are  $7500 \text{ \AA}$  and  $4800 \text{ \AA}$  for red and blue respectively.

Sol. Given that  $b = 3 \times 10^{-3} \text{ mK}$ ;  $\lambda = 7500 \text{ \AA}$ . Temperature of the body,  $T$

$$\therefore T = \frac{b}{\lambda} = \frac{3 \times 10^{-3}}{7500 \times 10^{-10}} = 4000^\circ \text{K}$$

$$\text{If } \lambda = 4800 \text{ \AA} \quad T = \frac{b}{\lambda} = \frac{3 \times 10^{-3}}{4800 \times 10^{-10}} = 6250^\circ \text{K}$$

9. Calculate the surface area of tungsten filament of 100 W electric bulb. The operating temperature of tungsten is  $2450 \text{ K}$  and its emissivity is  $0.3$ .

Sol. Given that  $E = 100 \text{ W}$

$$e = 0.3, \quad \sigma = 5.7 \times 10^{-8} \text{ W/m}^2/\text{K}^4, \quad T = 2450^\circ \text{K}$$

$$E = A \cdot e T^4$$

$$\begin{aligned} \text{Surface area of the filament is } A &= \frac{E}{e T^4} = \frac{100}{0.3 \times 5.67 \times 10^{-8} (2450)^4} \\ &= 1.63 \times 10^{-4} \text{ sq.m} = 1.63 \text{ sq-cm.} \end{aligned}$$

10. A body at  $1500 \text{ K}$  emits maximum energy at a wavelength  $20,000 \text{ \AA}$ . If the sun emits maximum energy at wavelength  $5500 \text{ \AA}$ . What would be the temperature of the sun.

Sol. Given that  $T_1 = 1500 \text{ K}$ ,  $\lambda_1 = 20,000 \text{ \AA}$ ,  $\lambda_2 = 5500 \text{ \AA}$ ,  $T_2 = ?$

From Wien's formula,

$$\lambda_1 T_1 = \lambda_2 T_2$$

$$\therefore T_2 = T_1 \times \frac{\lambda_1}{\lambda_2} = 1500 \times \frac{20000}{5500} = 5454.5^\circ \text{K}$$

11. What are the units of Wien's constant? Taking as  $2.85 \times 10^{-3} \text{ M.K.S. units}$ , find the temperature of the sun, if the wavelength corresponding to maximum emission is  $4753 \text{ \AA}$ .

Sol. The units of Wien's constant are  $\text{m-K}$

By Wien's displacement law,  $\lambda_m T = b$

$$\text{or } T = \frac{b}{\lambda_m} = \frac{2.85 \times 10^{-3}}{4753 \times 10^{-10}} = 5995^\circ \text{K}$$

12. Find the number of modes of vibration per unit volume in the wavelength region between  $4995 \text{ \AA}$  and  $5005 \text{ \AA}$  of a black body on Rayleigh Jeans law.

$$\text{Sol. Here } \lambda = \frac{4995 + 5005}{2} = 5000 \text{ \AA} = 5 \times 10^{-7} \text{ m}$$

$$d\lambda = 5005 - 4995 = 10 \text{ \AA} = 10^{-9} \text{ m}$$

$$N = \frac{8\pi}{\lambda^4} d\lambda$$

$$N = \frac{8 \times 3.14}{(5 \times 10^{-7})^4} \times 10^{-9} = \frac{8 \times 3.14}{25 \times 25} \times 10^{19} = 0.04019 \times 10^{19}$$

# PHYSICS PRACTICALS

## 1. Specific heat of a liquid - Joule's Calorimeter - Bartion's Radiation correction.

**Aim :** To determine the specific heat of liquid, using joules calorimeter.

**Apparatus :** Joule's calorimeter battery of constant e.m.f. ammeter, voltmeter, rheostat, sensitive balance, weight box, thermometer stop clock.

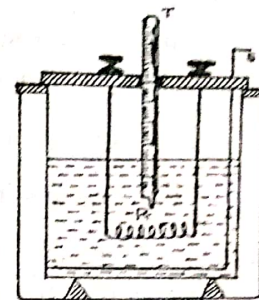
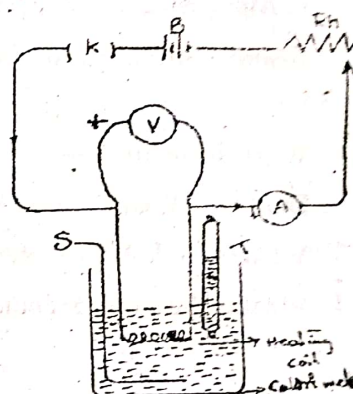


Fig.

**Description :** Joule's calorimeter consists of a cylindrical copper vessel closed by the non-conducting ebonite lid. To the lid the heating coil is connected and the binding screws are provided above hole lid. The thermometer can be introduced into the central hole provided in the lid. The calorimeter is enclosed in a non conducting box.

**Procedure :** The weight  $W_1$  of the empty calorimeter with stirrer in it is found. Taking water upto  $2/3$  of the calorimeter the weight  $W_2$  is found the calorimeter is placed in the non-conducting enclosure and the heating coil is introduced in the calorimeters

The battery is connected, in series with the Joule's heating coil ammeter, rheostat and plug key. The voltmeter is connected parallel to the heating coil. The key is closed and the rheostat is adjusted until the ammeter reads about 2 ampere. The key is removed and the initial temperature  $\theta_1$  of water in the calorimeter is noted. Then the key is closed and the stop clock started simultaneously and while passing current the ammeter reading  $C$  and voltmeter reading are noted. Then the temperature is noted for every 30 sec until the temperature rises about  $5^\circ\text{C}$ , then the current is stopped but the temperature is noted for every 30 sec until temperature falls about  $2^\circ\text{C}$ . Time  $t$  seconds during which the current is passed is noted.



Fig

**Bartion's Radiation correction :** A graph PQR is plotted taking time along x-axis and temperature along y-axis. The radiation correction (AB) can be calculated as follows. Lines QM and PL are drawn parallel to the x-axis at final and initial temperatures. A vertical line MNL is drawn parallel to y-axis, so that 'f' is greater than  $1^\circ\text{C}$ . Then areas on the curves A and B are calculated by counting small squares. Then Bartions radiation correction.

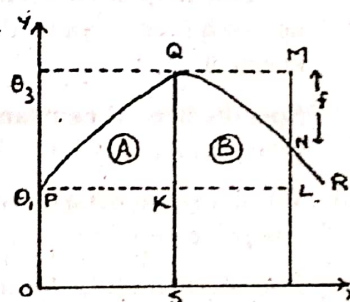


Fig.

$$\Delta \theta = \frac{A}{B} f$$

Then corrected final temperature  $\theta_2 = (\theta_3 + \Delta \theta)$

The work done due to current in the heater element (ECt) must be equivalent to the heat generated.

$$\therefore \frac{ECt}{J} = \{W_1 s + (W_2 - W_1) S\} (\theta_1 - \theta_2)$$

From the above formula, the specific heat of the liquid can be calculated.



**Observations :**

Weight of the calorimeter + stirrer ( $W_1$ ) = ..... gm

Weight of the calorimeter + stirrer + water ( $W_2$ ) = ..... gm

Initial temperature of water =  $\theta_1$  = .....  $^{\circ}\text{C}$

Ammeter reading =  $C$  = ..... amperes

Voltmeter reading =  $E$  = ..... Volts

Final temperature of water =  $\theta_3$  = .....  $^{\circ}\text{C}$

Final corrected temp of water =  $\theta_2$  = .....

Time during current is passed =  $t$  = ..... sec

Sp. heat of the material of the calorimeter =  $s$  = .....

Mechanical equivalent of heat =  $J$  = ..... Joules calorie

Sp. heat of liquid =  $s$  = .....

**Precautions :**

1. Thermometer should be removed with least loss of water.
2. Water should be stirred while passing current.
3. Ammeter and voltmeter should be further from the rheostant.

**Result :** Specific heat of the liquids  $S$  =

**Viva-Voce Questions**

1. What is specific heat ?
2. Define  $C_p$  &  $C_v$  ?
3. What is Joule-Kelvin effect ?
4. What is the value of Joule-Kelvin effect of a perfect gas ?

**Viva-Voce Answers**

1. The specific heat of a substance is the amount of heat required to raise the temperature of unit mass of the substance through  $1^{\circ}\text{C}$ .
2. **Specific heat at constant pressure ( $C_p$ ) :** The specific heat at constant pressure is the amount of heat required to raise the temperature of 1 gram gas through  $1^{\circ}\text{C}$  when the pressure is kept constant.  
**Specific heat at constant volume ( $C_v$ ) :** The amount of heat required to raise the temperature of 1 gram gas through  $1^{\circ}\text{C}$  when the volume is kept constant.
3. When a gas under a constant high pressure is passed through a porous plug to a region of constant low pressure
4. Joule-Kelvin effect for a perfect gas is zero.

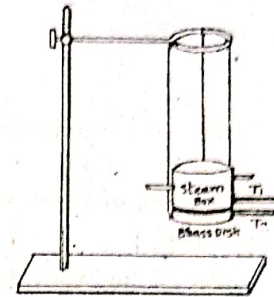
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## 2. Thermal Conductivity of bad Conductor - Lee's Method.

**Aim :** To determine the coefficient of thermal conductivity of a bad conductor by Lee's method.

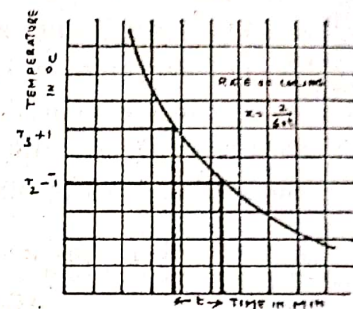
**Apparatus :** The Lee's apparatus, system generator, the given bad conductor in the form of a thin disc, two thermometers, stop watch, screw gauge, vernier calipers, a rough balance.

**Description :** The Lee's apparatus consists of a nickel coated brass disc (fig.) suspended with its plane horizontal by means of three strings tied to the ring of a retort stand. On the brass disc, the given bad conductor in the form of a thin disc of the same diameter as the brass disc is placed. And upon the bad conductor a brass steam chamber is placed and having the diameter as that of the bad conductor. The steam chamber is provided with an inlet and outlet for the passage of steam.



Fig

**Procedure :** i) The mass 'm' of the lower brass disc is found with a rough balance. The mean thickness  $d$  and the mean radius  $r$  of the lower brass disc are determined with a vernier calipers. The mean thickness  $t$  of the bad conductor is determined with the screw gauge.



Fig

ii) The bad conductor is placed in its proper position between the lower brass disc and the steam chamber. Steam is passed for a sufficiently long time until a steady temperatures of  $T_1^0$  C and  $T_2^0$  C respectively. In this steady state, heat is conducted across the bad conductor and received by the lower disc. The heat gained by conduction per second by the brass disc is equal to the heat lost by it per second due to radiation.

iii) The bad conductor is removed and the lower disc is directly put in contact with the steam chamber. The brass disc is heated until its temperature rises by about  $5^0$  above its steady temperature  $T_2^0$  C. The steam chamber is removed and the brass disc is allowed to cool. As the brass disc cools, its temperature is noted at intervals of half a minute until the temperature of the disc cools  $50^0$  C below the steady temperature  $T_2^0$  C. A cooling curve (Fig) is drawn showing the time intervals in minutes on the x-axis and the corresponding temperature on the y-axis. From the graph the time taken  $t$  minutes for the temperature to fall from  $(T_2 + 1)^0$  C to  $(T_2 - 1)^0$  C is noted. Then the rate of cooling  $\alpha$  at the steady temperature  $T_2^0$  C is found by

$$\alpha = \left( \frac{2}{60t} \right)^0 \text{ C/sec}$$

**Theory :** During the first part of the experiment, the heat conducted per sec by the bad conductor lower disc is

$$Q = \frac{k\pi r^2 (T_1 - T_2)}{t} \quad \dots(1)$$

Where  $K$  is the co-efficient of thermal conductivity of the bad conductor to be determined.

The quantity of heat radiated by the lower disc per second is

$$Q \propto m s \alpha^1 \quad \dots(2)$$

Where  $s$  is the specific heat of the lower disc and  $\alpha^1$  is the rate of cooling of the lower disc at the steady temperature  $T_2^0$  C.

$$\text{Hence } \frac{k\pi r^2 (T_1 - T_2)}{t} = m s \alpha^1 \quad \dots(3)$$



In this part of the experiment, the surface area of the lower disc exposed to radiation is  $\pi r^2 + 2\pi r d = \pi r(r + 2d)$ . In the second parts of the experiment, the surface area of the lower disc exposed =  $2\pi r^2 + 2\pi r d = 2\pi r(r + d)$ . Since the rate cooling is proportional to the surface area exposed,

$$\frac{\alpha^1}{\alpha} = \frac{\pi r(r + 2d)}{2\pi r(r + d)} = \frac{r + 2d}{2(r + d)} \quad \text{Or, } 1 = \frac{(r + 2d) \alpha}{2(r + d)} \quad \dots(4)$$

$$\text{From eqs (3) and (4)} \quad \frac{k\pi r^2(T_1 - T_2)}{t} = \frac{ms(r + 2d) \alpha}{2(r + d)} \quad \dots(5)$$

The value of k can be found by eq. (5)

#### Observations :

Mass of the brass disc (m) = ..... gm

Mean thickness of the lower disc (d) = ..... cm

Mean radius of the lower disc (r) = ..... cm

Mean thickness, of the bad conductor (t) = ..... cm

Steady temperature of Steam Chamber ( $T_1$ ) ..... =  $^{\circ}\text{C}$

Steady temperature of the lower disc ( $T_2$ ) = .....  $^{\circ}\text{C}$

Sp.heat of the lower disc (s) =

Rate of cooling ( from the graph =

$$\frac{k\pi r^2(T_1 - T_2)}{t} = \frac{ms(r + 2d) d}{2(r + d)}$$

**Precautions :** 1. The thickness of the bad conductor should be taken atleast in three different places. 2. Steam is passed for a sufficiently long time until there is no further change of the temperature  $0^{\circ}\text{C}$ .

**Result :** Co-efficient of thermal conductivity of the bad conductor (k) = ..... Cal/s/m $^{\circ}\text{C}$

#### Viva-Voce Questions

1. Define thermal conductivity K of a material.
2. Does the value of thermal conductivity K of a material depend upon the dimensions of the material in any way ?
3. What are the units of thermal conductivity ?
4. What is meant by temperature gradient ?
5. What are the units of temperature gradient ?

#### Viva-Voce Answers

1. Thermal conductivity of a material K is defined as the quantity of heat flowing per second normally through a unit area of cross section when the temperature gradient is unity.
2. No. K depends only on the material of the body and not on its dimensions.
3. Units of thermal conductivity are
  - a) In C.G.S. system cal/sec/cm $^2$ /unit temperature gradient or cal/sec/cm $^{\circ}\text{C}$
  - b) In SI the unit is W/m - K
4. Temperature gradient  $\frac{d\theta}{dx}$  means the fall of temperature along unit length.
5. Units of temperature gradient are
  - a) in C.G.S. = .....  $^{\circ}\text{C}/\text{cm}$
  - b) in SI = ..... K/m

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### 3. Thermal Conductivity of Rubber.

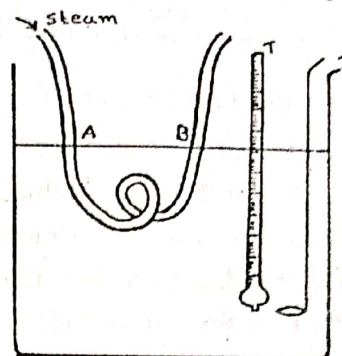
**Aim :** To determine the co-efficient thermal conductivity of rubber.

**Apparatus :** Rubber tubing, steam generator, Bunsen, burner, a stop watch, balance, weight box, calorimeter, thermometer.

**Description :** The large rubber tubing is made into a coil in the middle and the coil portion is immersed into the water contained in the calorimeter. One end of the rubber tubing is connected to the steam generator and the other end is projected a little outside the calorimeter.

**Procedure :** The calorimeter is cleaned, dried and weighed together with the stirrer. Let it be  $w_1$  gm. Suitable quantity of water is taken in the calorimeter and the weight of the calorimeter + stirrer + water is found. Let it be  $w_2$  gm. The watch is well stirred and its initial temperature  $\theta_1$  °C is noted.

The coil portion of the rubber tubing is immersed in water. Two cotton threads (A and B in the figure) are tied round the rubber tubing, one where it enters the water and the other where it leaves the water.



Fig

Steam is generated in steam generator when dry steam is issuing its temperature  $\theta_2$  °C is noted. It is then passed through the rubber tubing for a time  $t$  (until the temperature of water rises by about 10° C) and the final maximum temperature  $\theta_3$  °C of water is noted.

The rubber tubing is removed from the calorimeter and the length  $l$  of the rubber tubing between A and B is found by a meter scale. The inner radius  $r_1$  and the outer radius  $r_2$  of the rubber tubing are found by the travelling microscope.

**Theory :** The amount of heat conducted by the rubber tubing in a time  $t$  is

$$Q = \frac{k \times 2\pi l (\theta_2 - \theta_2^1) t}{2.3026 \log_{10} \left( \frac{r_2}{r_1} \right)}$$

where  $k$  is the co-efficient of thermal conductivity of rubber to be determined  $\theta_2^1$  is the average temperature of the calorimeter and its contents, or

$$\theta_2^1 = \frac{\theta_1 + \theta_3}{2}$$

This heat is gained by the cal + stirrer + water. Hence

$$Q = (W_1 s + W_2 - W_1) (\theta_3 - \theta_1)$$

Where  $s$  is the known specific heat of the calorimeter

$$\text{Hence } \frac{k \times 2\pi l t \left[ \theta_2 - \frac{\theta_1 + \theta_3}{2} \right]}{2.3026 \times \log_{10} \left( \frac{r_2}{r_1} \right)}$$

$$= (W_1 s + W_2 - W_1) (\theta_3 - \theta_1)$$

from which  $k$  can be determined

**Observations :**

Weight of the cal + stirrer ( $W_1$ ) = ..... gm



Weight of the cal + stirrer ( $W_1$ ) = ..... gm  
 Weight of the cal + stirrer + water ( $W_2$ ) ..... gm  
 Initial temperature of water ( $\theta_1$ ) = ..... °C  
 Temperature of steam ( $\theta_2$ ) = ..... °C  
 Resultant temperature of water  $\theta_3$  = ..... °C  
 Sp heat of the Calorimeter (s) = .....  
 Length of the rubber tubing ( $l$ ) = ..... cm  
 Inner radius of rubber tubing ( $r_1$ ) = ..... cm  
 Outer radius of rubber tubing ( $r_2$ ) = ..... cm  
 Time of flow of heat ( $t$ ) = ..... sec

$$\frac{k \times 2\pi l t \left[ \theta_2 - \frac{\theta_1 + \theta_3}{2} \right]}{2.3026 \times \log_{10} \left( \frac{r_2}{r_1} \right)} = (W_1 s + W_2 - W_1) (\theta_3 - \theta_1)$$

**Precautions :**

1. The rubber tubing should be of uniform thickness.
2. The inner and outer radii of the rubber tubing should be determined very accurately, reading taken along to mutually perpendicular diameters.
3. The cotton loops tied round the tubing should be kept touching the free surface of water in the calorimeter.

**Result :** Co-efficient of thermal conductivity of rubber ( $k$ ) = ..... cal/sec/cm<sup>2</sup>/°C

**Viva-Voce Questions**

1. Define thermal conductivity  $K$  of a material.
2. Does the value of thermal conductivity  $K$  of a material depend upon the dimensions of the material in any way ?
3. What are the units of thermal conductivity ?
4. What is meant by temperature gradient ?
5. What are the units of temperature gradient ?

**Viva-Voce Answers**

1. Thermal conductivity of a material  $K$  is defined as the quantity of heat flowing per second normally through a unit area of cross section when the temperature gradient is unity.
2. No.  $K$  depends only on the material of the body and not on its dimensions.
3. Units of thermal conductivity are
  - a) In C.G.S. system cal/sec/cm<sup>2</sup>/unit temperature gradient or cal/sec/cm<sup>2</sup>/°C
  - b) In SI the unit is  $W/m - K$
4. Temperature gradient  $\frac{d\theta}{dx}$  means the fall of temperature along unit length.
5. Units of temperature gradient are
  - a) in C.G.S. = ..... °C/cm
  - b) in SI = ..... K/m

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#### 4. Measurement of Stefan's constant.

**Aim :** To measure in the laboratory, the value of Stefan's Constant  $\sigma$ .

**Apparatus :** The simple apparatus designed to determine the value of  $\sigma$ , the Stefan's constant, three thermometers -  $T_1$  and  $T_2$  to be kept in the Wooden box B and  $T_3$  in the tube of oil O, a stop watch.

**Formula :** 1. Stefan's constant  $\sigma = \frac{Jms}{A(\theta_1^4 - \theta_2^4)} \cdot \frac{dT}{dt}$  ....(1)

and  $\frac{dT}{dt} = \frac{dT}{d\theta} \cdot \frac{d\theta}{dt}$  ....(a)

With  $\frac{dT}{d\theta} = \tan \alpha$  and  $\frac{d\theta}{dt} = \tan \beta$  we get  $\sigma = \frac{Jms}{A(\theta_1^4 - \theta_2^4)} \frac{\tan \alpha}{\tan \beta}$  ....(2)

Units of  $\sigma$  are (a) watts/cm<sup>2</sup> - degree<sup>4</sup> or W cm<sup>-2</sup> degree<sup>-4</sup> in C.G.S. system.

(b) W. m<sup>2</sup>K<sup>-4</sup> in SI

In this formula (with C.G.S units)  $J$  = Joule's constant = Mechanical equivalent of heat = 4.18 J / Cal (In SI,  $J = 1$ )

$m$  = mass of the silver (or copper) disc in grams

$s$  = specific heat of the silver (or copper) disc in cal/gramm-°C

$\frac{dT}{dt}$  = rate of raise of temperature of the disc (°C/s)

$A$  = area of the upper surface of the disc (cm<sup>2</sup>)

$\frac{dT}{d\theta}$  = Difference of hot junction (E) temperature of the thermo couple and the temperature of cold junction (disc) (rooms temperature)  $\div$  Corresponding difference in Galvanometer deflection

$$\frac{d\theta}{dt} = \frac{\text{Difference in deflection in the galvanometer}}{\text{time interval}}$$

$\theta_1$  is the absolute temperature of the enclosure A in Kelvin and

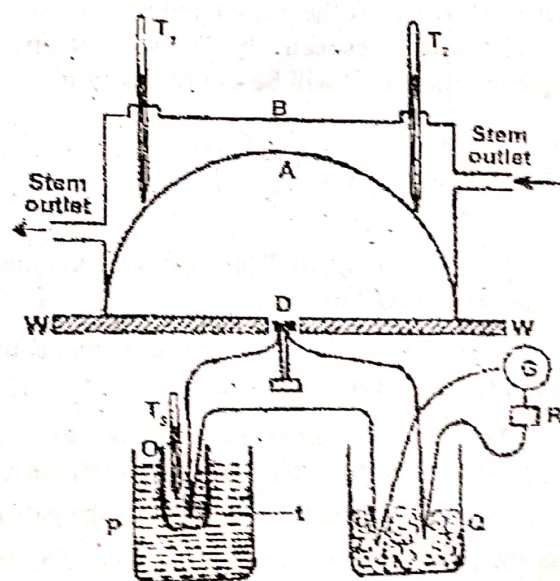
$\theta_2$  is the absolute temperature of the disc D in kelvin

The values of  $m$ ,  $s$  and  $A$  are constants of the (apparatus) instrument and the manufactures of the instrument (apparatus) provide us with the values.

**Description of Experiment :** The laboratory apparatus used in laboratory to determine Stefan's constant ( will be as shown in fig

A hollow hemispherical metallic vessel A of diameter 25 cm is enclosed in a wooden box B. The inner surface of A is coated with lamp black and the wooden box B is lined with tin plates. The whole apparatus is placed on a wooden base W - W having a small hole of diameter 2.5 cm at its centre. The vessel A is heated by passing steam inside the box and A acts as a black body radiator. The thermometer  $T_1$  record the temperature of A.

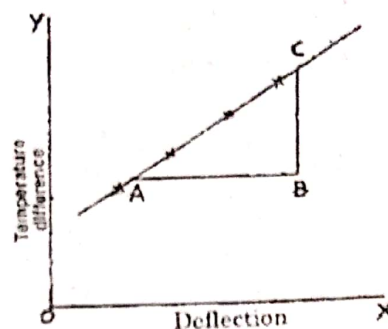
A small silver or copper disc  $D$  whose upper surface is coated with lamp black is placed at the central hole. The ebonite covering  $C$  is used to cover and uncover the disc  $D$  from the radiations of the enclosure.





It can be arranged from outside with the help of the handle  $H$ . The disc  $D$  is connected to a thermocouple arrangement. The thermo couple is silver-constantan thermo couple. One junction of the thermocouple is immersed in a tube  $O$  containing oil. The tube  $O$  is surrounded by a beaker  $P$  containing water. A sensitive galvanometer  $G$  is used in the circuit. The leads connected to the terminals of the galvanometer are immersed in cotton wool in the box  $Q$  to avoid any distribution effect due to the difference of temperature in the leads. A rheostat  $RB$  can be used in the circuit to obtain the deflection within the range if necessary. The actual experiment consists of two parts.

1. The thermo couple is first standardized. Before passing steam into the chamber the disc  $D$  is the room temperature the water bath  $P$  acts as a hot junction. It is heated and at various temperatures of the hot junction, the corresponding deflections ( $\theta$ ) in the galvanometer are noted. A graph between the difference of temperature of the hot junction and the room temperature along the y-axis and galvanometer deflection along X-axis is plotted (Fig)



From the graph,

$$\frac{dT}{d\theta} = \tan \alpha = \frac{AB}{BC} \quad \dots(3)$$

2. The disc  $D$  is completely covered with  $C$  and steam is passed into the chamber. After some time, the thermometers  $T$  and  $T$  show constant temperature. The bath  $E$  is kept at room temperature. With the help of the handle  $H$ , the cover  $C$  is tilted so that the upper surface of the disc  $D$  receives the radiations from the enclosure. The deflections in the galvanometer are observed at equal intervals of time

(say 10 seconds). A graph is plotted between time and deflection (fig.3). A tangent is drawn on the curve at a point  $P$ .

$$\frac{dt}{d\theta} = \tan \beta = \frac{EF}{GF} \quad \dots(4)$$

### Procedure :

**1. Standardization of the Thermo couple :** Before passing any steam through the wooden box, the disc  $D$  will be at the room temperature. The steady temperatures of the two  $T_1$  and  $T_2$  are noted down in  $^{\circ}\text{C}$  as  $t_1$  and  $t_2$  respectively. The room temperature  $t^{\circ}\text{C}$  will be the mean of  $t_1^{\circ}\text{C}$  and  $t_2^{\circ}\text{C}$ . The thermo couple junction at  $D$  will be a cold junction.

$$\text{That is } t_{\text{room}} = \left( \frac{t_1 + t_2}{2} \right)^{\circ}\text{C}$$

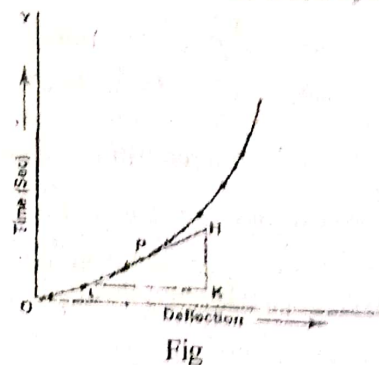
The disc  $D$  and the Hemisphere  $A$  are now at this room temperature  $t^{\circ}\text{C}$ . The junction at disc  $D$  at  $t^{\circ}\text{C}$  acts as the cold junction.

The tube of oil  $O$  can be heated by heating the beaker of water  $P$ . The thermo couple junction  $E$  inside  $O$  acts as a hot junction.

The water beaker is heated slowly and steadily, there by heating the oil and consequently heating the junction  $E$  of the thermo couple. Temperature  $t_j$  of the hot junction is noted from thermometer  $T_j$  in  $^{\circ}\text{C}$ . As the hot junction is heated slowly, the galvanometer deflections ( $\theta$ ) will also increase. The deflection  $\theta$  in the galvanometer is noted for every  $5^{\circ}\text{C}$  temperature raise of the hot junction  $E$ . Thus we get

galvanometer deflection ( $\theta$ ) for various temperature differences of hot and cold junctions of the thermo couple  $T = (t_3 - t)^{\circ}\text{C}$ .

A graph is drawn with difference of temperature of thermo couple junctions ( $T = (t_3 - t)^{\circ}\text{C}$ ) on y-axis and corresponding galvanometer deflections ( $\theta$ ) on the x-axis. The graph will be shown in fig.2



From this graph  $\frac{dT}{d\theta} = \tan \alpha = \frac{AB}{BC}$  is easily found ....(9)

2. The second part consists of determining  $\frac{dt}{d\theta}$  so that  $\frac{dT}{dt} = \frac{dT}{d\theta} \cdot \frac{d\theta}{dt}$  can be calculated and substituted in the formula. The tube of oil  $O$  along with water beaker  $P$  is cooled down to room temperature.

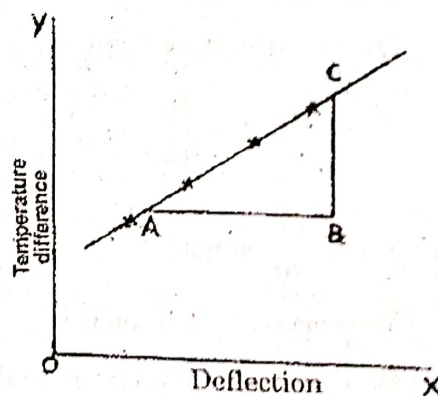
The disc  $D$  is completely covered with ebonite covering  $C$ . Steam is passed into the wooden box  $B$ . After some time, the two thermometers  $T_1$  and  $T_2$  will be showing constant [(and nearly equal) temperatures of about  $100^{\circ}\text{C}$ ] temperatures  $t_4^{\circ}\text{C}$  and  $t_n^{\circ}\text{C}$  respectively for more than 5 minutes. The mean temperature

of the hemisphere  $A$  (which is acting as a radiator) will be  $\left(\frac{t_3 + t_4}{2}\right)^{\circ}\text{C}$ . But, we should express this temperature in Stefan's Law as  $\theta_1$  in absolute or Kelvin scale.

$$\text{That is } \theta_1 = \left[ \left( \frac{t_3 + t_4}{2} \right) + 273 \right]$$

As the tube oil  $O$  is now at room temperature, the junction  $E$  of the thermo couple now acts as a cold junction.

Now, with the help of the handle  $H$ , the ebonite cover  $C$  is tiffed to be outside the disc  $D$  ( $D$  is uncovered) such that the upper surface of  $D$  receives the heat radiations from the heat radiator, that is the hemisphere  $A$ . As the disc receives the heat, it will raise in temperature and hence  $D$  will now act as a hot junction whereas the junction  $E$  acts now as the cold junction. Again the deflections ( $\theta$ ) in the galvanometer will be increasing. The stop clock is started and the deflections ( $\theta$ ) are noted down for every 10 seconds of time interval. A graph is plotted with time  $t$  (in seconds) on y-axis and corresponding deflections ( $\theta$ ) on x-axis. The graph will come out as in fig.3.



On this curve a point  $P$ , not far from the origin is taken. A tangent to the curve is drawn at the point  $P$  and from this, as shown in fig - 3, the value of

$$\frac{dt}{d\theta} = \tan \beta = \frac{EF}{GF} \text{ is calculated}$$

....(11)

From equations (9) and (11).



$$\frac{dT}{dt} = \frac{dT}{d\theta} \cdot \frac{d\theta}{dt} = \frac{\tan \alpha}{\tan \beta} \quad \dots(12)$$

Now, we have still to find out the temperature  $\theta_2$  the absolute temperature of the disc  $D$ . For this we have to first notice from fig-3, the deflection  $\theta_p$  corresponding to the point  $P$ . For this deflection, the temperature  $T_p$  is noted from fig-2. To this value  $T_p$  in degree Celsius add the room temperature  $t^\circ\text{C}$  and convert the result into absolute (or Kelvin) temperature.

$$\theta_2 = (T_p + t) + 273$$

Substituting the appropriate values in Equation

$$\sigma = \frac{Jms}{A(\theta_1^4 - \theta_2^4)} \frac{\tan \alpha}{\tan \beta}$$

We get the value of Stefan's constant  $\sigma$ .

**Observations :** 1. The values of the following will be specified by the manufacturer of the apparatus. They are mass of the silver (or copper disc),  $m = \dots\dots\dots$  grams.

Specific heat of the silver (or copper disc),  $s = \dots\dots\dots$  cal/gram  $^\circ\text{C}$

Area of the upper surface of the disc,  $A = \dots\dots\dots\text{cm}^2$

2. For  $\frac{dT}{d\theta}$  graph. Junction  $E$  is heated and junction at  $D$  kept at room temperature

Difference of hot junction ( $E$ ) temperature and cold junction (disc $D$ ) temperature (room temperature) $T$ in $^\circ\text{C}$				
Galvanometer deflection $\theta$ in degrees				

$T$  on  $y$ -axis. Scale 1 cm =  $\dots\dots\dots$

$D$  on  $x$ -axis scale 1 cm =  $\dots\dots\dots$

$$\frac{dT}{d\theta} = \tan \alpha = \frac{AB}{BC} = \dots\dots\dots$$

3. For  $\frac{dt}{d\theta}$  graph.

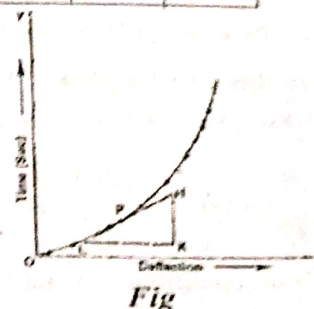
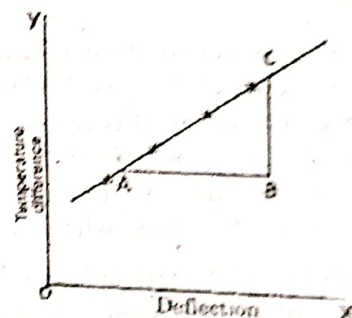
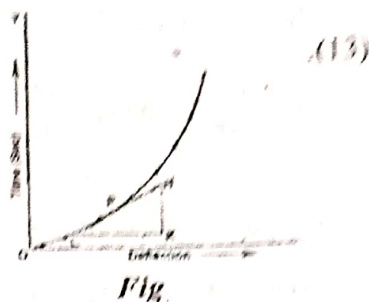
Time interval $t$ in seconds						
Galvanometer deflection $\theta$ in degrees						

$t$  on  $y$  axis. Scale 1 cm =  $\dots\dots\dots$

$\theta$  on  $x$  axis scale 1 cm =  $\dots\dots\dots$

$$\frac{dt}{d\theta} = \tan \beta = \frac{EF}{GF} = \dots\dots\dots$$

4. To find  $T_2$  and  $\theta_2 = T_2 + 273$ . Deflection corresponding to point  $P$  in fig 3 =  $\theta_p$



Temperature difference  $T$  for  $\theta_p$  from fig - 2 = .....  $t_p$

$\theta_2$  = in Kelvin =  $t_p$  + room temp (t) + 273

**Calculations :** Stefan's constant  $\sigma$  is found from above observations from the formula

$$\sigma = \frac{Jms}{A(\theta_1^4 - \theta_2^4)} \frac{\tan \alpha}{\tan \beta}$$

(a) If  $m$ ,  $s$  and  $A$  pre specified in C.G.S units, then are have to substitute  $J = 4.18 \text{ J/cal}$  and  $\sigma$  will be in  $\text{watts/cm}^2 - \text{degree}^4$ .

(b) If  $m$ ,  $s$  and  $A$  are in SI units,  $J = 1$  and  $\sigma$  will be in  $\text{watts/m}^2 - \text{K}^4$  or  $\text{Wm}^2 \text{K}^{-4}$ .

**Result :**  $\sigma$  = ..... in  $\text{W/cm}^2 - \text{degree}^4$   
 = ..... in  $\text{Wm}^2 \text{K}^{-4}$

#### Precautions :

1. The upper surface of the disc  $D$  and the lower surface of the hemisphere  $A$  are to be perfectly blackened. This is because Stefan's law  $E = \sigma T^4$  or  $E = \sigma (T^4 - T_0^4)$  is true for a perfectly black body only.

2. The galvanometer should be insulated from heat radiations.

3. When the disc  $D$  is heated by radiation from  $A$ , in the beginning the galvanometer deflections increase rapidly. Therefore initially time interval should be very small  $\sim 2$  or  $3$  seconds only.

**Source of Error :** In this experiment, the following are the main sources of error.

1. The temperature of the radiator - that is, the metal hemisphere may not attain a fixed constant value.

2. The mercury thermometers  $T_1$  and  $T_2$  that are usually employed in our laboratory are not quite sensitive. For this, we can make use of platinum resistance thermometers that are more sensitive.

3. Here we are assuming the emitter or radiator (metal hemisphere) as well as the absorber (silver or copper disc  $D$ ) to be perfectly black bodies. In actual practice, they are not so. As such the entire thermal radiation falling on the disc  $D$ , may not be absorbed by it in full in increasing its temperature.

#### Viva-Voce Questions

1. What is Stefan's Law of thermal radiation ?
2. What is Boltzmann Law ?
3. What is Stefan - Boltzmann Law ?
4. What is Stefan's constant  $\sigma$  ?
5. How does  $\sigma$ , Stefan's constant depend on the wavelength of thermal radiation ?

#### Viva-Voce Answers

1. Stefan's Law states that the total heat radiation (of all wavelengths) per second from unit surface area of a perfect black body is directly proportional to the fourth power of absolute temperature of the body.

$$\frac{Q}{A} = E \propto T^4 \text{ or } E = \sigma T^4$$

2. The Stefan's Law is derived theoretically by Boltzmann and Boltzmann's law is the same as Stefan's Law.

3. The law  $E = \sigma T^4$  is itself called Stefan-Boltzmann law. Thus all the three names stand for the same law.

4. Let the total energy (of all wavelengths) radiated per second from unit surface area of a perfectly

black body be  $\frac{Q}{A} = E$  at an absolute temperature  $T$  of the body According to Stefan's Law.

$$E \propto T^4 \text{ or } E = \sigma T^4$$

The proportionality constant  $\sigma$  is called the Stefan's constant.

5. Stefan's constant  $\sigma$  does not depend on the wavelength of thermal radiation. It applies to the entire whole range of all wavelengths.

—O—



## 5. Specific heat of a liquid by applying Newton's Law of Cooling correction.

**Aim :** To determine the specific heat  $x$  of a given liquid by applying Newton's Law of cooling.

**Apparatus :** A calorimeter coated with lamp black on the outside completely, the given liquid whose specific heat is to be determined, a sensitive thermometer that can read correct upto  $0.1^\circ\text{C}$  difference of temperature and having a range from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ , a stop clock, a sensitive physical balance with weight box.

**Formula :** 1. If  $x$  is the specific heat of the given liquid,  $x$  can be calculated from the formula

$$\frac{W_1 s + (W_2 - W_1)}{t_w} = \frac{W_1 s + (W_3 - W_1)}{t_L}$$

Units of  $x$  = .....cal/gram  $^\circ\text{C}$ .

Where  $W_1$  = weight of empty calorimeter along with stirrer (in grams)

$s$  = Specific heat of the material of calorimeter (and stirrer) in cal/gram  $^\circ\text{C}$ .

$W_2$  = Weight of calorimeter with stirrer with water (in grams)

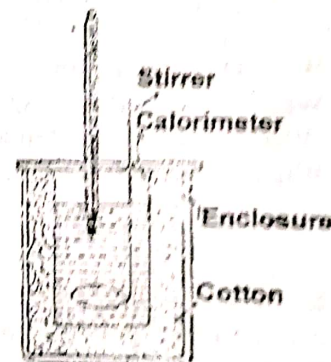
$t_w$  = time taken by hot water inside the calorimeter to cool from  $\theta_1^\circ\text{C}$  to  $\theta_2^\circ\text{C}$  (in seconds)

$W_3$  = weight of calorimeter with stirrer with the given liquid (in grams)

$t_L$  = time taken by hot liquid inside calorimeter to cool from same  $\theta_1^\circ\text{C}$  to  $\theta_2^\circ\text{C}$  (in seconds)

**Units :**  $x$  will be in cal/gram  $^\circ\text{C}$

**Description :** The calorimeter used in this experiment is shown in fig -1. It is a cylindrical copper vessel containing a stirrer of the same material. It is provided with a non-conducting lid having two holes. The sensitive thermometer is passed through one hole. Through the other hole the stirrer is passed. For this particular experiment, the entire outside surface of the calorimeter is completely coated with lamp black so that the calorimeter along with contents inside acts as a black body radiator.



**Theory of the experiment :** The rate at which thermal radiation is radiated from a black body depends upon 1. The area of the radiating surface, 2. The nature of the radiating surface, that is its emissivity, 3. The mean excess of the temperature of the hot body over the temperature of the enclosure or surroundings. When we keep the first two factors remaining the same, the rate of loss of heat by the radiating surface will be directly proportional to the mean excess of temperature of the body over the surroundings. This is actually called Newton's Law of cooling.

Now, let the calorimeter (with stirrer) of weight  $W_1$  having hot water of weight  $W_2 - W_1$  at a temperature  $\theta_1^\circ\text{C}$  be left in the open air to cool to a temperature  $\theta_2^\circ\text{C}$ . Let the time taken for this cooling be  $t_w$  seconds. The rate of loss of heat by calorimeter and contents (water) is therefore,

$$\left( \frac{dQ}{dt} \right)_w = \frac{[W_1 s + (W_2 - W_1)] (\theta_1 - \theta_2)}{t_w}$$

Here  $s$  is the specific heat of the calorimeter and stirrer. Specific heat of water is one. This is because, specific heat of  $(W_2 - W_1)$  grams water is 1 cal/gram  $^\circ\text{C}$ .

Next, let the calorimeter be filled (to the same extent as water) with the given liquid be raised to a high temperature (about  $\theta_1^\circ \text{C}$ ) and left in the open air to cool. Let the time taken to cool from  $\theta_1^\circ \text{C}$  to  $\theta_2^\circ \text{C}$  be now  $t_L$  seconds. In this case the rate of cooling by calorimeter with hot liquid is given by

$$\left( \frac{dQ}{dt} \right)_L = \frac{[W_1 s + (W_3 - W_1) x] (\theta_1 - \theta_2)}{t_L}$$

This is because, specific heat of  $[(W_3 - W_1) \text{ gm}]$  of liquid is  $x$ .

As the area of the radiating surface (outside surface of calorimeter), and the mean excess of temperature  $(\theta_1 - \theta_2)^\circ \text{C}$  are the same in both the cases we have The rate of loss of heat is the same in both cases And hence it follows

$$\frac{[W_1 s + (W_2 - W_1)] (\theta_1 - \theta_2)}{t_W} = \frac{[W_1 s + (W_3 - W_1) x] (\theta_1 - \theta_2)}{t_L}$$

That is 
$$\frac{W_1 s + (W_2 - W_1)}{t_W} = \frac{W_1 s + (W_3 - W_1) x}{t_L}$$

**Procedure :** First of all the weight  $W_1$  of the empty calorimeter along with the stirrer (but not the lid) is determined with the sensitive physical balance. The readings are entered in table-1. Next the calorimeter and stirrer are placed on a non-conduction stand. A suitable amount of water (so as to fill  $\frac{2}{3}$  of the calorimeter, say) is taken in a vessel and is heated upto  $90^\circ \text{C}$ . A mark is placed on the inner side of the calorimeter at a height some what a little less than  $\frac{2}{3}$  the height of the calorimeter. The hot water is gently poured into the calorimeter upto this fixed mark. The lid is closed on the calorimeter and the stirrer and thermometer are inserted. When the temperature of the hot water is just  $80^\circ \text{C}$ , the stop clock is started and the temperature is noted down at regular intervals of time, say for every 15 seconds. This is continued until the temperature falls upto  $50^\circ \text{C}$ . The calorimeter and contents are allowed to cool upto the room temperature. Then the weight  $W_2$  of the calorimeter along with stirrer and water is determined. Readings are tabulated in table - 1.

The water is completely poured out of the calorimeter. The inside of the calorimeter is cleaned thoroughly with a blotting paper and a clean dry cloth. It is then placed on the non-conducting stand. The given liquid, whose specific heat  $x$  is to be determined is taken (so as to have approximately more than  $\frac{2}{3}$  volume of the calorimeter) in a separate vessel and is heated upto  $90^\circ \text{C}$ . It is then gently poured into the calorimeter just upto the same fixed mark. After closing the lid the stirrer and thermometer reading is  $80^\circ \text{C}$  and the temperatures at same regular intervals of time (15 seconds) are noted upto  $50^\circ \text{C}$ .

Calorimeter and the liquid is allowed to cool upto room temperature and the weight  $W_3$  of the calorimeter with stirrer and liquid is determined with the balance. Readings are tabulated in table - 1.

By taking the water and the liquid both upto the fixed mark we are ensuring that the same volume is taken.

**Observations and Graph :** 1. Weights  $W_1$ ,  $W_2$  and  $W_3$  are determined with a sensitive balance and taking the weight nearer to the zero resting point (Z.R.P) as the correct weight. These readings are entered in the following table - 1



Table - 1

S.No.	Object in Left Pan	Mass in Right Pan	Turning Points		Average		Resting Point $\left(\frac{a+b}{2}\right)$
			Left (3)	Right (2)	Left (a)	Right (b)	Z.R.P.
1	0	0					
2 (W <sub>1</sub> )	Calorimeter						
	Calorimeter						
3 (W <sub>2</sub> )	Calorimeter + Water						
	Calorimeter + Water						
4 (W <sub>2</sub> )	Calorimeter + Liquid						
	Calorimeter + Liquid						

2. Time - Temperature readings for drawing cooling curves.

(A) For water

Time : (In seconds)	0	15	30	45	60	75
Temperature (In °C)	80	-	-	-	-	-

(B) For given liquid :

Time : (In seconds)	0	15	30	45	60	75
Temperature (In °C)	80	-	-	-	-	-

3. Two cooling curves, that is graphs with time on  $x$ -axis and corresponding temperature on  $y$ -axis one for water and the other for the given liquid are drawn on the same graph sheet.

A. For water :

Scale on  $x$  - axis (time) 1 cm =

Scale on  $y$  - axis (temperature) 1 cm =

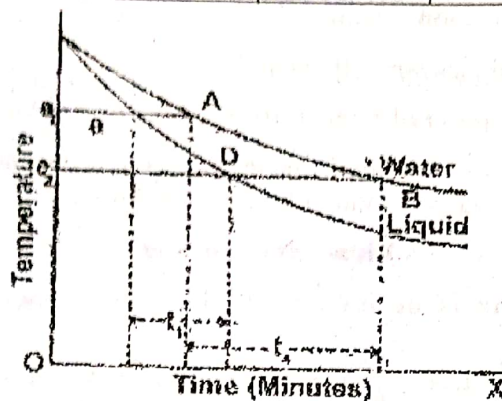
Time (seconds)						
Temperature (°C)						

B. For liquid :

Scale on  $x$ -axis (time) 1 cm =

Scale on y-axis (temperature) 1 cm =

Time (seconds)						
Temperature ( $^{\circ}\text{C}$ )						



Fig

The curves will be as show in Fig.2

From these graphs, the times  $t_w$  and  $t_L$  taken by the water and the liquid respectively to cool from  $\theta_1^{\circ}\text{C}$  to  $\theta_2^{\circ}\text{C}$  are determined as shown in the graph.

4. The weights and other data are written as follows

Weight of the calorimeter with stirrer,  $W_1 = \dots\dots\dots$  gm

Weight of the calorimeter + water with stirrer,  $W_2 = \dots\dots\dots$  gm

Weight of the calorimeter + liquid with stirrer,  $W_3 = \dots\dots\dots$  gm

Specific heat of water =  $\dots\dots\dots = 1 \text{ cal/gm-}^{\circ}\text{C}$

Specific heat of material calorimeter and s stirrer that is, that of copper  $s = \dots\dots\dots \text{cal/gm-}^{\circ}\text{C}$

Time taken by water to cool from  $\theta_1^{\circ}$  to  $\theta_2^{\circ}\text{C} = t_w = \dots\dots\dots \text{s}$

Time taken by liquid to cool from  $\theta_1^{\circ}$  to  $\theta_2^{\circ} = t_L = \dots\dots\dots \text{s}$

#### Calculations :

Formula used to calculate x, the specific heat of the given liquid

$$\frac{W_1 s + (W_2 - W_1)}{t_w} = \frac{W_1 s + (W_3 - W_1) x}{t_L}$$

#### Result :

Specific heat of the given liquid  $x = \dots\dots\dots \text{cal/gm-}^{\circ}\text{C}$ .

#### Precautions :

1. The water and the liquid are to be taken exactly to the same fixed mark-same height in the calorimeter. This is quite essential to ensure that same volume of water and liquid are taken.
2. The temperature difference between the calorimeter and contents and the surroundings should be small. Preferably should be less than  $50^{\circ}\text{C}$ .



3. In still air the excess should be limited to be with in  $20^{\circ}\text{C}$  or  $30^{\circ}\text{C}$ . However in a draught (forced convection) the excess can be higher, such as  $50^{\circ}\text{C}$

### Viva-Voce Questions

1. One of the precautions to be taken in the experiment is that the temperature difference between the calorimeter and contents and the surroundings should be small. Why is this condition necessary?
2. Define specific heat and mention its units.
3. Which liquid has got the highest specific heat ?
4. What is meant by "mean excess of temperature" of the body over its surroundings ?
5. Can we apply Newton's law of cooling if the temperature difference between the hot body and the enclosure or surrounding is large ? Which law is to be applied in such a situation ?

### Viva-Voce Answers

1. Newton's law of cooling is derived from the more general Stefan-Boltzmann's Law

$\frac{dQ}{dt} = R = \sigma A (T^4 - T_0^4)$  Here  $\frac{dQ}{dt} = R$  is the rate at which the hot body is losing heat by radiation,  $\sigma$  is Stefan's constant,  $A$  is the area of the radiating surface,  $T$  is the absolute temperature of the hot body and  $T_0$  is the absolute temperature of the surroundings or enclosure.

Now, for unit surface area, the rate of loss of heat is

$$E = \sigma (T^4 - T_0^4) = \sigma (T^2 + T_0^2) (T + T_0) (T - T_0) \text{ and when } T - T_0 \text{ is small we can have}$$

$$T + T_0 = T_0 \text{ and } E = 4 \sigma T_0^3 (T - T_0)$$

Here  $4 \sigma T_0^3$  is a constant and hence  $E \propto (T - T_0)$ . This is Newton's law of cooling. However, here we assumed  $T - T_0$  is small. And hence, the condition is required.

2. Specific heat is the amount of heat required to raise the temperature of unit mass of the substance through unit temperature. In C.G.S. system unit of specific heat is  $\text{cal/gm}^{\circ}\text{C}$  and in SI the unit is  $\text{joule/kg}^{\circ}\text{C}$ .
3. Out of liquids, water has got the highest specific heat of  $1 \text{ cal/gm}^{\circ}\text{C}$  or  $4280 \text{ joules/kg}^{\circ}\text{C}$ .
4. Let us suppose that originally the hot body is at a temperature  $\theta_1$  and temperature of the surroundings  $\theta_0$ . In a time 't' the hot body cools to a temperature  $\theta_2$ . The mean excess of temperature of the

body over surroundings is  $\frac{\theta_1 + \theta_2}{2} - \theta_0$ . The rate of cooling, according to Newton's law is

$$\frac{dT}{dt} \propto \left[ \frac{\theta_1 + \theta_2}{2} - \theta_0 \right]$$

5. No. Then we have to apply Stefan - Boltzmann Law.

## 6. Heating efficiency of electrical kettle with varying voltages.

**Aim :** Varying the applied voltage, to determine the efficiency of the electric kettle at different voltages.

**Note :** Usually an electric kettle operates at 230 V having a rating of some kilowatts. To adjust the rheostat and making connections at such a high A.C. value will be dangerous and hence, in our laboratories we usually do the experiment with a Joule's Calorimeter, applying 6 V D.C and determine the efficiency of the heater element.

**Apparatus :** A Joule calorimeter (in place of the electric kettle), D.C. voltmeter and D.C. ammeter, a storage battery of 6 V emf, connecting wires, rheostat, plug key, sensitive balance, stop clock.

**Formula :** The heating efficiency of the heater element (kettle)

$$\eta = \frac{[W_1 s + (W_2 - W_1)] (\theta_2 - \theta_1) \cdot J}{V i t} \times 100 \text{ percent}$$

Here  $W_1$  = mass of empty calorimeter ..... in gm

$W_2$  = mass of calorimeter with water ..... in gm

$s$  = specific heat of the material of the calorimeter in cal/gm-°C.

(as the Joule's Calorimeter is usually made of aluminium,  $s = 0.22 \text{ cal/gm-}^\circ\text{C}$ )

$\theta_1$  = temperature of water inside the calorimeter before passing any current in °C

$\theta_2$  = temperature of water inside the calorimeter after passing of current for  $t$  seconds ..... in °C.

$t$  = time of passage of current in seconds

$V$  = voltage applied

= Voltmeter reading ..... in volts.

$i$  = electric current passing through the heater element

= ammeter reading ..... in amperes.

$J$  = mechanical equivalent of heat

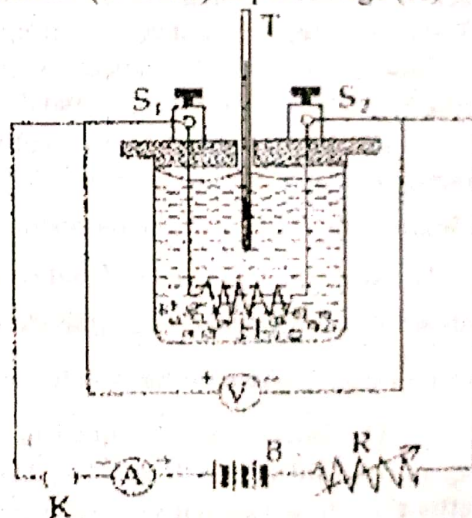
= 4.18 joules/calorie

$\eta$  = Heating efficiency of the heater element in joules calorimeter (or kettle) in percentage (%)

### Description :

Joule calorimeter is a special kind of calorimeter used in the laboratory used to determine the value of  $J$ , the mechanical equivalent of heat. This is shown in fig - 1.

Unlike an ordinary calorimeter (made of copper) this is made with aluminium. We do not require the stirrer here. This calorimeter is kept inside a wooden box having a hole. The lid covering this hole is made of a bad conductor of heat, like ebonite. This lid will be just covering the calorimeter also. There will be two binding screws  $S_1$  and  $S_2$  on the lid. The lower parts of these two binding screws will be each connected to a thick copper rod extending down the lid (but not upto the bottom of the calorimeter when it is covered with the lid). The lower ends of the rods will be connected by a nichrome wire. This nichrome wire is the





heating element. Usually the lid will be having two holes having covered tightly with two corks having holes. Through one hole a thermometer is inserted. The thermometer should go down inside the calorimeter. Through the second hole the stirrer is to be passed. But in the present experiment, there is no need for a stirrer and hence we close down the second hole tightly and completely.

The ammeter ( $A$ ) and voltmeter ( $V$ ) used in this experiment are D.C.meters. A rheostat  $R$  is used to change the current in the circuit.  $B$  is storage battery of 6V.

The outer surface of the calorimeter is brightly polished to minimise the loss of heat due to radiation. The space between the calorimeter and the wooden box is packed with cotton or felt to minimise the loss of heat due to conduction.

**Theory of the experiment :** The work done by the current ( $i$ ) passing through the heating element at a voltage ( $V$ ) during a time ( $t$ ) is given by

$$W = Vit \text{ (joules)} \quad \dots(1)$$

The heat gained by the calorimeter and water is  $Q = [W_1s + (W_2 - W_1)] (\theta_2 - \theta_1)$  (calories) ... (2)

This heat  $Q$  will be equivalent to a work of  $H = Q \times J = \text{joules}$  ... (3)

Hence we expect  $J [W_1s + (W_2 - W_1)] (\theta_2 - \theta_1) = Vit$  ... (4)

But, this is possible only when the heating element (kettle) operates with hundred percent (100%) efficiency. But a percent efficiency is impossible.

The efficiency is given by  $\eta = \frac{\text{output energy}}{\text{input energy}} \times 100 \text{ (Percent)}$

$$\text{(i.e.)}, \eta = \frac{H}{Vit} \times 100 = \frac{Q \times J}{Vit} \times 100$$

$$\eta = \frac{J [W_1s + (W_2 - W_1)] (\theta_2 - \theta_1)}{Vit} \times 100 \quad \dots(5)$$

**Procedure :** With the help of the sensitive balance, the mass ( $W_1$ ) of the empty calorimeter is determined first. Then water is poured about two thirds of the calorimeter - such that, when the ebonite lid is placed on the calorimeter, the heating element gets sufficiently immersed inside the water. The mass ( $W_2$ ) of the calorimeter with water is now determined. The readings are tabulated in Table - 1.

Now, the calorimeter is placed inside the wooden box and the lid is tightly closed. The thermometer ( $T$ ) is now inserted into the calorimeter through the hole in the lid. Care should be taken to see that the bulb of the thermometer goes down sufficiently inside the water.

The storage battery  $B$ , rheostat  $R$ , ammeter  $A$  and plug key  $K$  are arranged in series and connected across the two binding screws  $S_1$  and  $S_2$ . The voltmeter  $V$  is connected in parallel, between  $S_1$  and  $S_2$ . The connecting wire coming out from the positive terminal (+) of the battery should be connected to the (+) positive terminal of ammeter. As we are coming to  $S_1$  in series from + positive terminal of battery, we should connect the positive terminal of voltmeter to  $S_1$ .

First we have to make use of 6 V P.D across the heating element  $H$ . Closing the plug key, the rheostat is adjusted to get 6 V P.D across the heating elements  $t$ . The key is opened. Then after five minutes, the reading of the thermometer ( $\theta_1$ ) is noted.

Next, the key is closed and simultaneously the stop clock is started. After a temperature raise of about  $5^\circ\text{C}$  (i.e.,  $\theta_2 - \theta_1 + 5$ ) the stop clock is stopped, and the key is opened. The time taken for this ( $5^\circ\text{C}$ ) raise of temperature is noted as  $t$  seconds. Obviously  $\theta_2 = \theta_1 + 5^\circ\text{C}$ .

The values are substituted in equation - 1 and the value of  $\eta$  is calculated. The experiment is again repeated with 5 V and 4 V P.D. across the heating element  $H$  with the help of the rheostat. The efficiency  $\eta$  is calculated at different voltages.

## Observations :

## (1) Balance :

Table - 1

S.No.	Object in Left Pan	Mass in Right Pan	Turning Points		Average		Resting Point $\left(\frac{a+b}{2}\right)$
			Left (3)	Right (2)	Left (a)	Right (b)	
1	0	0					Z.R.P
2	Calorimeter						
	Calorimeter						
3	Calorimeter + Water						
	Calorimeter + Water						

Note : For each measurement of weight of any object, we should have one higher resting point (H.R.P) (greater than zero resting point Z.R.P) and one lower resting point (L.R.P) (less than Z.R.P) Of these H.R.P & L.R.P. one will be nearer to Z.R.P. The mass of the object corresponding to that resting point is to be taken as the mass of the object (correct to a centigram).

- A) 1. Mass of empty calorimeter,  $W_1 = \dots\dots\dots$  gm  
 2. Mass of calorimeter + Water,  $W_2 = \dots\dots\dots$  gm  
 3. Specific heat of material of calorimeter,  $s = \text{cal/gm}^\circ\text{C}$

B) Experiment with  $V = 6V$  :

1. Initial temperature  $\theta_1 = \dots\dots\dots$   $^\circ\text{C}$   
 2. Voltmeter reading,  $V = \dots\dots\dots$  V  
 3. Ammeter reading,  $i = \dots\dots\dots$  A  
 4. Time of passage of current,  $t = \dots\dots\dots$  s  
 5. Final temperature,  $\theta_2 = \dots\dots\dots$   $^\circ\text{C}$   
 6. Mechanical Equivalent of heat,  $J = 4.18 \text{ J/Cal}$

Efficiency of the heating element at 6 V

$$\eta = \frac{J [W_2 s + (W_2 - W_1)] (\theta_2 - \theta_1)}{V i t} \times 100$$

$$= \dots\dots\dots\%$$

Similarly :

(C) With  $V = 5 V$ 

1. Initial temperature,  $\theta_1 = \dots\dots\dots$   $^\circ\text{C}$   
 2. Voltmeter reading,  $V = \dots\dots\dots$  V  
 3. Ammeter reading,  $i = \dots\dots\dots$  A  
 4. Time of passage of current,  $t = \dots\dots\dots$  s



5. Final temperature,  $\theta_2 = \dots\dots\dots ^\circ\text{C}$
6. Mechanical Equivalent of heat,  $J = 4.18 \text{ J/Cal}$
- Efficiency of the heating element at  $5V$

$$\eta = \frac{J [W_1 s + (W_2 - W_1)] (\theta_2 - \theta_1)}{V i t} \times 100$$

$$= \dots\dots\dots \%$$

**D) With  $V = 4 \text{ V}$**

1. Initial temperature,  $\theta_1 = \dots\dots\dots ^\circ\text{C}$
2. Voltmeter reading,  $V = \dots\dots\dots \text{V}$
3. Ammeter reading,  $i = \dots\dots\dots \text{A}$
4. Time of passage of current,  $t = \dots\dots\dots \text{s}$
5. Final temperature,  $\theta_2 = \dots\dots\dots ^\circ\text{C}$
6. Mechanical Equivalent of heat,  $J = 4.18 \text{ J/Cal}$
- Efficiency of the heating element at  $4 \text{ V}$

$$\eta = \frac{J [W_1 s + (W_2 - W_1)] (\theta_2 - \theta_1)}{V i t} \times 100$$

$$= \dots\dots\dots \%$$

**Result :**

The efficiency of the heating element at different voltages is as follows.

S.No.	Voltage (V)	Efficiency $\eta$ (percentage)
1.	6 V	
2.	5 V	
3.	4 V	

**Precautions :** The following precautions are to be carefully observed during this experiment.

1. The voltage (V) and current (i) should remain constant throughout the experiment.
2. The thermometer insertion should be done very carefully, taking care to see that no heat flows out through the hole through which the thermometer is inserted.
3. Water is to be filled in the calorimeter such that the heating element gets sufficiently well immersed inside the water.
4. In the electrical circuit, the ammeter (A) should be connected in series and the voltmeter (V) in parallel.

#### Viva-Voce Questions

1. What is meant by the efficiency of a device.
2. In the formula for  $\eta$ , we have multiplied  $W_1$  with 's' but, we did not multiply  $(W_2 - W_1)$  with 's', Why ?
3. What is specific heat of a substance ?
4. Which liquid has the highest specific heat ?
5. What is the value of specific heat of water in (a) C.G.S system and (b) Si

## Viva-Voce Answers

1. When we supply any device with a certain amount of energy (as input), the device either does some work utilising this energy or converts the energy into another form and releases it (as output). However the entire input energy can never be converted as work or into equivalent output energy. Due to several reasons, some of the input energy gets wasted or unutilized.

The capability of a device to convert the input energy into output energy is termed as its efficiency.

$$\text{Percentage efficiency } \eta = \frac{\text{output energy}}{\text{input energy}} \times 100$$

2.  $W_1 \times s$  is called the water equivalent of the calorimeter. When this quantity is multiplied by  $(\theta_2 - \theta_1)$  we get the heat required to raise the temperature of the calorimeter from  $\theta_1$  to  $\theta_2$ .

But for water, the specific heat  $s = 1$  (in C.G.S system) and hence  $(W_2 - W_1)$  will itself be the water equivalent.

3. The specific heat of a substance is the amount of heat required to raise the temperature of unit mass of the substance through  $1^\circ\text{C}$ .

4. Water.

5. (a) In C.G.S system  $s = 1 \text{ Cal/gm-}^\circ\text{C}$

(b) In SI  $s = 4200 \text{ J/kg-}^\circ\text{C}$

ater in SI is  $4200 \text{ J/kg-}^\circ\text{C}$  and hence  $(W_2 - W_1)$  should be multiplied by 4200 in the formula.

—O—



## 7. Thermo E.M.F. - Thermo Couple - Potentio Meter.

**Aim :** To determine the E.M.F. of a thermo couple for various temperature differences between the junctions using a potentio meter.

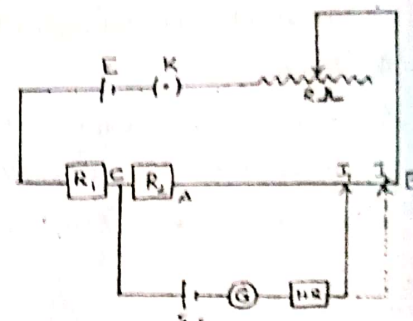
**Apparatus :** Potentiometer, Batteries, Standard cadmium cell, two resistance boxes, plug key, sensitive galvanometer, thermo couple (Copper-constant couple or copper-iron couple) two water baths thermometer.

**Procedure :** When a circuit is composed of two dissimilar metal junctions and junctions are maintained at different temperatures, an E.M.F is developed in the circuit. The e.m.f. is called thermo e.m.f. Keeping one of the junctions at constant temperature and heating the other junction slowly, the thermo e.m.f. gradually increases until it reaches a maximum value and there after decreases.

The experiment consists of three parts.

- Determination of the resistance of potentiometer wire.
- Calibration of potentiometer.
- Measurement of e.m.f. of the thermo couple.

**i) To determine the resistance (r) of the potentiometer wire**  
 The primary circuit, with a battery E, plug key K, a rheostat Rh, and two resistance boxes  $R_1$ ,  $R_2$  are connected in series with a potentiometer wire AB. Then the (+ve) terminal of the standard cell (S.C) is connected to the junction C between  $R_1$  and  $R_2$  and the negative pole the jockey J of the potentiometer meter through a galvanometer 'G' and a high resistance H.R. as shown in fig.



Fig

In the resistance box  $R_2$  a value of J (say 5 ohm) is plugged out keeping  $R_1 = 0$ . The primary circuit is closed and the balance point  $J_1$  is found. The balancing length  $l_1$  and  $AJ_1$  wire is measured.

The resistance of same value 'r' (say 5 ohms) is plugged out from  $R_1$  and resistance in  $R_2$  is kept zero and the balance point  $J_2$  is found. The balancing length  $l_2$  of the portion  $AJ_2$  of the potentiometer wire is measured.

Then the resistance of  $(l_2 - l_1)$  c.m. of the wire is equal to 'r' ohms. Hence the resistance of entire length of the potentiometer wire is given by

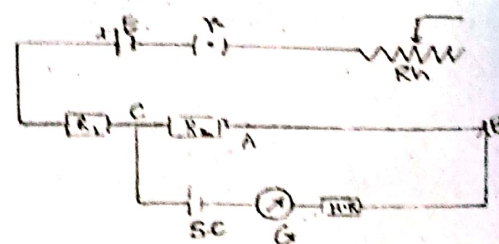
$$P = \frac{r}{(l_2 - l_1)} \times 1000 \text{ ohms}$$

The experiment is repeated for different values of 'r' and in each case the resistance P of the potentiometer wire is determined. (Resistance 'r' must always be less than the resistance of the potentiometer wire). The readings are tabulated.

**ii) Calibration of the potentiometer wire :** The connections are made as shown in fig. AB is the potentiometer wire of resistance P ohms. The standard cell S.C. of E.M.F. 'E' volts is balanced across A.B.

If it is desired that the fall of potential per millimeter length of the potentiometer wire should be 1 micro volt, then the P.D. between the ends of the potentiometer wire should be

$$10^{-6} \times 10,000 = 10^{-2} = \frac{1}{100} \text{ volts}$$



Fig

If  $I$  is the current in primary circuit and  $R$  the resistance the box  $R_2$  then.

$$\text{The P.D. between A and B} = IP = \frac{1}{100} \text{ volt}$$

$$\text{The P.D. between C and B} = 1 (P + R) = E \text{ volts}$$

$$\therefore \frac{R + P}{P} = E \times 100$$

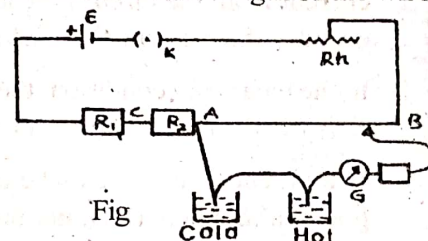
$$\therefore R = P (100 E - 1)$$

The resistance in the box  $R_2$  is given a value equal to  $P (100E - 1)$ . The resistance in the box  $R_1$  is adjusted until the galvanometer shows zero deflection when jockey is pressed at B'. If necessary the resistance in the reostat  $R_h$  may also be adjusted to get zero deflection in the galvanometer. The standard cell is now balanced across  $(R + P)$ .

The potentiometer is thus calibrated so that the fall of potential across 1 m.m. length of the wire is 1 micro volt.

### iii) Measurement of the E.M.F. of the thermo couple :

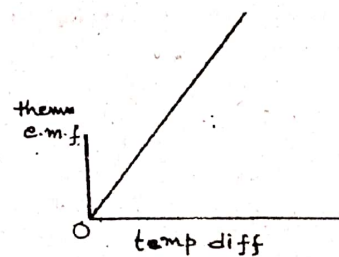
Without disturbing the primary circuit, the standard cell in the secondary circuit is removed and in its place a thermo couple is connected as in fig with a galvanometer and a jockey J in series.



The cold junction is maintained at a constant temperature by keeping it in a water bath kept at room temperature. The hot junction is kept in another water bath and heated slowly. When the temperature of the hot junction is  $10^\circ \text{C}$  above that of the cold junction, the water bath is kept constant at that temperature and balance point is located. The temperature is noted and the balancing length 1 m.m from the +ve end of the potentiometer wire is measured. Then the thermo e.m.f. corresponding to the difference of temperature  $\theta$  is 1 microvolts.

The experiment is repeated for every  $10^\circ \text{C}$  rise of temperature until the boiling point of water is reached. The thermo e.m.f. at each step corresponding to the difference of temperature is also determined.

A graph is drawn with difference temperature along the X-axis and the corresponding thermo e.m.f. along the Y-axis. For small difference in temperature between cold and hot junctions is almost a straight line as in fig.



Fig

### Observations :

E.M.F. of the cell  $E = \dots\dots\dots$  volts

Resistance of the potentiometer wire  $P = \dots\dots\dots$  ohms.

The value of  $R = P (100E - 1) = \dots\dots\dots$  ohms

Temperature of cold junction  $= ^\circ\text{C}$

S.No.	Temp	Diff. in temperature $\theta$	Balancing length 1 m.m	Thermo e.m.f. in micro volts	Thermo e.m.f. per degree diff. of temp $1/\theta$



## Viva-Voce Questions

1. For determination of potential differences and emfs, potentiometer is more accurate than a voltmeter. Why ?
2. What is the principle of a potentiometer ?
3. The sensitivity of a potentiometer is high. Why ?
4. What is the potential gradient in a potentiometer ? What are its units ?
5. What is the material with which the potentiometer wire is made ? What is the reason for it ?

## Viva-Voce Answers

1. The construction of an ideal voltmeter having infinite resistance is impossible. Hence, while measuring p.d. with a voltmeter, the voltmeter will be drawing some current from the circuit. This makes the p.d. across the resistor ( $V = iR$ ) to be less than the actual  $iR$  drop. With a potentiometer, such a problem will not arise at all because, in the balancing condition, the potentiometer draws no current from the circuit. Hence, the actual p.d. will be measured. Hence, potentiometer is a more accurate instrument than V.M. in measuring P.D. or emf.
2. In the balancing condition, the value of P.D. ( $E$ ) will be proportional to the balancing length ' $l$ ' (i.e.)  $E \propto l$  is the potentiometer principle.
3. In a potentiometer we make use of a wire of total length  $10 \times 100 = 10,000 \text{ cm}$ . This makes the potential gradient (P.D. per unit length) very small. Hence, even very small P.D.s can be accurately measured. This makes a potentiometer more sensitive than a metre bridge.
4. The potential drop per unit length of the potentiometer wire is called its potential gradient. Its units are volts/centimetre ( $V/\text{cm}$ ).
5. The potentiometer wire is made of either manganin or constantan. This is because, these materials have high specific resistance (or resistivity) and low temperature coefficient of resistance.

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## 8. Thermal behavior of an Electric Bulb (Filament/ Torchlight Bulb)

**Aim :** To study the variation of resistivity of the tungsten filament and measurement of temperature of the filament.

**Apparatus :** 5 Volts regulated power supply, Digital voltmeter with 200 mV/0-20V dual range. Digital ammeter with 0 - 2000  $\mu$  A/0-2A dual range. Electric bulb (Torch) operating at 6 Volts.

**Formula :** Resistance of the filament at temperature  $T^\circ\text{K}$  ( $R_T$ ) is given by

$$R_T = \frac{R_0 \rho_T}{\rho_0}$$

$R_0$  = Resistance of the wire at room temperature (300 K)

$\rho_T$  = Resistivity at the temperature.

$\rho_0$  = Resistivity of the filament at room temperature ( $=5.65 \mu \Omega \cdot \text{cm}$ )

Formula for measurement of Temperature (T)  $T = 3.05 \times 10^8 \times \rho^{0.83}$

**Measurement of resistivity of metal wire and its temperature :** The resistance (R) of a wire of uniform radius is given by

$$R = \rho \frac{L}{A_c}$$

L = length of the wire

$A_c$  = Cross - Sectional area of the wire

$\rho$  = Resistivity

Generally length of the wire and its cross sectional area temperature dependent. However, the percentage variations in length and cross sectional area of tungsten wire are estimated to be around 2% for a temperature of 3000 K. Hence the more appropriate to describe in the temperature dependence of resistance of wire is given by

$$R_T = R_0 \frac{\rho_T}{\rho_0}$$

$R_T$  = Resistance of wire at temperature "T" K.

$R_0$  = Resistance of wire at room temperature

$\rho_T$  = Resistivity of wire at temperature "T"

$\rho_0$  = Resistivity of wire at room temperature.

Temperature of the filament is given by

$$T = (3.05 \times 10^8) \rho_T^{0.83}$$

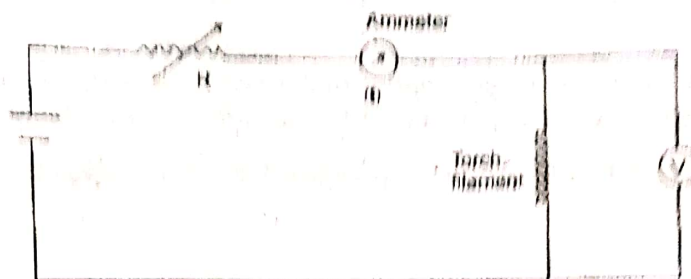
Here "T" is in Kelvin.  $\rho$  is in  $\Omega \cdot \text{m}$

**Experimental procedure :** The experiment consists of two parts. In the first part, the resistance of the cold filament is determined by passing a small current through the filament. In the second part, the resistance of the heated filament is determined by passing a large current so that the bulb glows. The



temperature of the film is then calculated using equation (4)

1. The bulb is fitted in the socket and the circuit connections are made as shown in figure below.



**Fig Circuit connection for measuring resistance of filament**

2. Connect  $1k\Omega$  resistor in the place of 'R' in series with bulb, and note down the ammeter (in  $\mu A$  range) and voltmeter (in mV) reading. Repeat the same with  $2k\Omega$  and  $3k\Omega$ . Due high resistance (or low current) the bulb does not glow. Hence the filament remains cold and therefore its resistance is constant.

Resistance of the cold filament or resistance of filament at room temperature ( $R_0$ ) is estimated as  $R_0 = \dots\dots\dots \Omega$

3. To determine the resistance of the filament at different temperatures, the power (current and voltage) is varied so that the bulb glows. This is done by connecting resistors of low value in series with the bulb. To do this we need a set of resistors  $1\Omega, 2\Omega, \dots, 8\Omega, 10\Omega, 20\Omega, \dots, 30\Omega$ .

#### Observations :

Table - 1 : For the measurement of resistance of cold filament,

Sl.No.	Resistor connected in the circuit (in series with bulb)	Voltage across bulb mV (V)	Current passing through the filament ( $\mu A$ )	Resistance of the cold filament ( $R_0$ )

Average ( $R_0$ ) =  $\dots\dots\dots \Omega$

Table - 2 : For the measurement of resistance of Hot filament,

Sl.No.	Resistor connected in series with bulb	Voltage across bulb mV (V)	Current passing through the filament ( $\mu A$ )	Resistance of the hot filament ( $\Omega$ ) ( $R_T$ )

Average ( $R_T$ ) =  $\dots\dots\dots \Omega$

Table - 3 : For the measurement of temperature of filament.

Resistance of hot filament ( $\Omega$ )	Resistivity $\mu \Omega / cm$	Temperature of filament

**Note :** Maximum temperature of filament is around 2132 K.

**Result :** The temperature of filament under maximum glow condition is ..... K.

4. Connect  $1 \Omega$  resistor in series with the bulb, and the current flowing through the filament voltage across the filament is noted. In this case bulb glows. Calculate the resistance of the filament (at that temperature) with that current  $I$  and voltage ( $V$ ) value.

5. Repeat the same procedure by connecting all other resistors in series with the bulb and calculate resistance of the filament at those temperatures. Tabulate then in a table - 2.

6. Resistivity of the filament at different temperature is calculated by rearranging equation (3) and enter the observation in Table - 3.

$$\rho_T = \rho_0 \frac{R^T}{R_0}$$

7. Substitute the value of  $\rho_T$  in equation (4) to get the temperature of the filament ; at that resistivity.

#### Precautions :

1. The connections should be made carefully having no loose contacts.
2. The resistances should be of non-inductive type.
3. The connecting wire ends should be scrubbed with sand paper.
4. The connecting wires should be short in length and straight.

#### Viva-Voce Questions

1. On what principle does the meters work ?
2. Then, how can you measure p.d. also with such an arrangement ?
3. Why an ammeter is connected in series in the circuit ?
4. What is the resistance of an ideal ammeter ?
5. Why so ?

#### Viva-Voce Answers

1. These meters work on the principle that a current carrying coil placed in a magnetic field gets deflected and the deflection is proportional to the current.
2. This is possible because, according to Ohm's law the current is proportional to the p.d.
3. This is because, the current to be measured should actually pass in full through the meter.
4. An ideal ammeter should have zero resistance.
5. Because, the resistance of the ammeter ( $R_A$ ) if any, adds to the resistance  $R$  of the circuit and the

current gets altered as  $\frac{V}{R + R_A}$  instead of being  $\frac{V}{R}$  only.

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## 9. Measurement of Stefan's Constant - Emissive Method.

**Aim :** To determine the Stefan-Boltzman constant by studying the radiation received from a black body radiator.

**Apparatus :** Blackened hemisphere (metal), heating coil, blackened silver disc, thermocouple, power supply, stop clock etc.

**Formula :** Stefan's constant is given by

$$\sigma = \frac{J m S}{A (T_1^4 - T_2^4)} \frac{dT_2}{dt}$$

$T_1$  = Temperature of black body radiator.

$T_2$  = Temperature blackened silver disc which receive radiation.

$m$  = mass of silver disc

$S$  = Specific heat of the disc

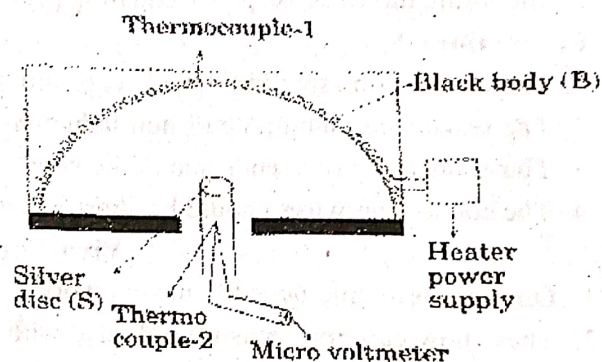
$A$  = Area of the disc

$\frac{dT_2}{dt}$  is the rate of change of temperature of the disc.

$J$  = Joules equivalent =  $(4.2 \times 10^7 \text{ ergs/calorie})$

**Experimental Setup :** The experimental setup (Fig-1) consists of a blackened hollow hemisphere which could be heated to a uniform temperature ( $T_1$ ) by passing electric current through a nichrome heating element wound over it.

The black body could be maintained at any desired constant temperature upto about  $200^\circ\text{C}$  by passing appropriate current through heating coil. A copper constant an thermocouple-1 connected to outer surface of "B" is used to ensure that temperature of the body is constant before starting the experiment. A blackened silver disc is used to measure its temperature.



### Procedure :

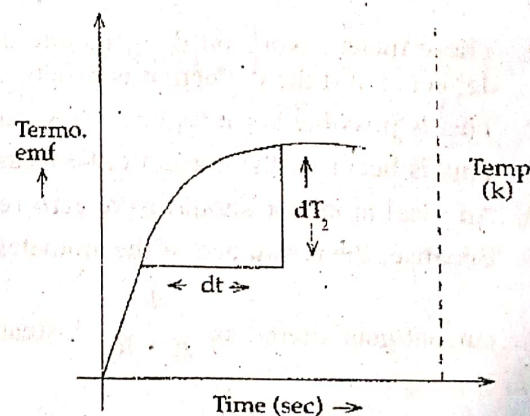
1. Heat the black body (B) to a uniform temperature (usually heating will be started before you come to the lab). Ensure that the temperature of the black body is constant by monitoring the thermo e.m.f developed by the thermocouple-1 for few minutes. (Ignore small fluctuations in micro voltmeter display).

2. Insert a thermometer through the hole provided for the disc "S" carefully and measure the temperature  $T$ , of the black body.

3. Replace thermometer with the silver disc carefully and mount it properly (make sure that disc is at room temperature before inserting).

4. Record the thermo e.m.f. of thermocouple-2 developed as a function of time (say at 10 sec interval).

5. Note down the mass and diameter of the disc.



6. Convert the thermo e.m.f. to temperature ( $T_2$ ) by using calibration chart for it.

7. Plot  $T_2$  as a function of time, obtain  $\frac{dT_2}{dt}$  from the data and calculate the value of  $C$ . Specific heat of the silver disc at room temperature  $S = 0.235 \text{ J/Kg-K}$ .

**Observations :**

1. Mass of the disc.
2. Diameter of the disc.
3. Temperature of the black body ( $T_1$ ) =
4. Temperature of the disc ( $T_2$ ) =

Table for recording thermo e.m.f. as function of temperature :

Sl.No.	Time (Sec)	Thermo e.m.f. (mV)	Temperature K
1	10		
2	20		
3	30		
:	:		
10	100		
:	:		

Plot  $T$  Vs time and find slope, and use equation (2) to Calculate ( $\sigma$ )

**Result :** Measured value of  $\sigma =$

**Precautions :**

1. The connections should be made carefully having no loose contacts.
2. The resistances should be of non-inductive type.
3. The connecting wire ends should be scrubbed with sand paper.
4. The connecting wires should be short in length and straight.

**Viva-Voce Questions**

1. What is Stefan's law ?
2. What are the units of Stefan's constant ?
3. Define Kirchoff's law.
4. What is the expression for Wien's law ?
5. What is Rayleigh-Jean's law ?

**Viva-Voce Answers**

1. The total amount of radiant energy by a black body per unit area per second due to all wave length is directly proportional to the forth power of absolute temperature is  $E \propto T^4$  (or)  $E = \sigma T^4$
2.  $\text{W m}^{-2} \text{K}^{-4}$
3. At a given temperature, the ratio of emissive power to the absorption power for a given wavelength is the same for all bodies and is equal to the emissive power of a black body at the same temperature.
4.  $\lambda_m T = \text{constant}$ .

5.  $E_\lambda = \frac{8\pi K^T}{\lambda^4}$

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## 10. Study of variation of resistance with temperature Thermistor.

- Aim :** 1) To draw the resistance - temperature and the voltage current characteristics of a thermistor.  
2) To evaluate constants in the formula for resistance variation with temperature.

**Apparatus :** Thermistor  $2K \Omega$  ;  $1K$  resistance - 2 (1 watt) or 2 resistance boxes (1 to  $100000 \Omega$ )

1 variable resistance box.

1 storage cell (2V).

1 table galvanometer.

**Theory :** Thermistor is a temperature - sensitive semi conductor with high negative temperature coefficient of resistance. They are made up of mixtures of metallic oxides such as manganese, nickel, cobalt, copper etc. Their resistance varies from  $0.5 \Omega$  to several kilo ohms.

The resistance of a thermistor varies with temperature according to the relation.

$$R = A_e B/T \quad \dots(1)$$

Where A and B are constants and T is the absolute temperature. The constants A and B are characteristics of the thermistor used.

Fig

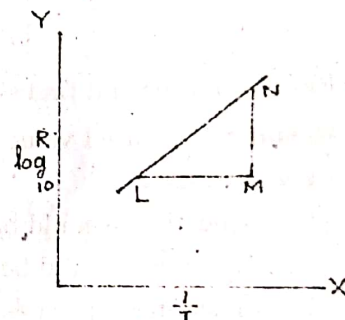
Taking logarithms on both sides

$$\log_e R = \log_e A + \frac{B}{T} \quad \dots(2)$$

$$(or) 2.303 \log_{10} R = 2.303 \log_{10} A + \frac{B}{T}$$

$$\log_{10} R = \log_{10} A + 0.4343 \frac{B}{T} \quad \dots(3)$$

A graph is between  $\log_{10} R$  and  $\frac{1}{T}$ . It is a straight line graph as shown fig.



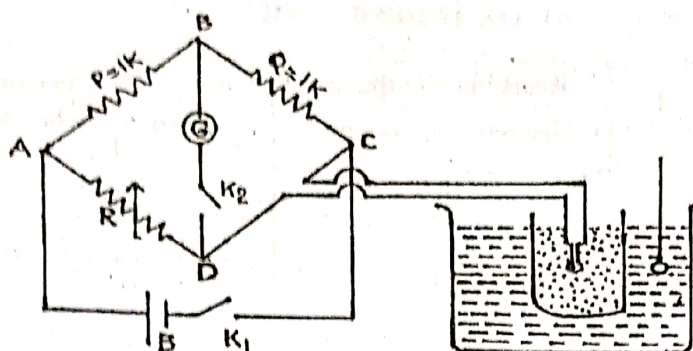
The slope  $\frac{MN}{LN}$  gives the value of  $0.4343B$ . Hence B can be calculated knowing the value of B, the constant A can be calculated from the formula

$$\log_{10} A = \log_{10} R - 0.4343 \frac{B}{T} \quad \dots(4)$$

If R is known at temperature (T).

By finding the resistance (R) at a known temperature (T), substituting the value of B, in the above equation A can be found.

**Procedure :** The thermistor is connected in the fourth arm 'S' of the wheat stonis bridge as shown in fig.



Fig

In the two arms P and Q resistances 1 K each are placed and in the third arm R a variable resistance box is connecting. The thermistor is placed in a test tube containing some oil and it is then placed in water bath as shown.

The bridge is balanced by adjusting the variable resistance box. The resistance in the third arm R gives the resistance of the thermistor at room temperature. Similarly the resistance is found at various temperatures in steps of  $10^\circ\text{C}$ . The water bath is cooled and the resistance of the thermistor is found again at the temperatures at which the resistances are found while heating. The average resistance at each step is calculated.

A graph is drawn taking temperature (in  $^\circ\text{A}$ ) in X-axis and resistance on Y-axis. The graph gives temperature characteristic of the thermistor.

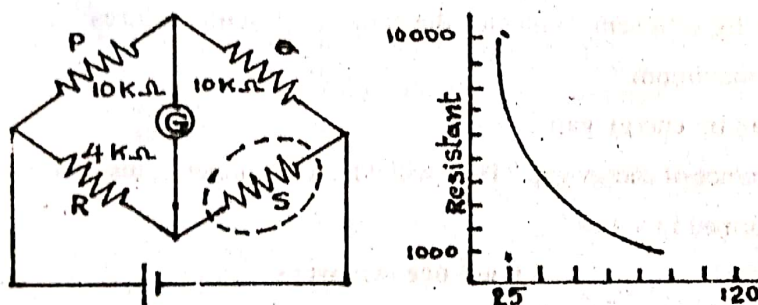
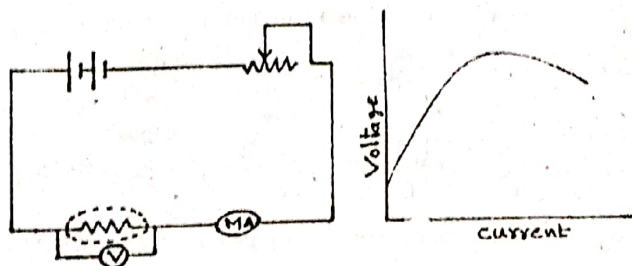


Fig.

Another graph is drawn with  $\frac{1}{T}$  on X-axis and  $\log_{10} R$  on Y-axis fig. The slope  $\frac{MN}{LM}$  gives the value 0.4343B. Hence B is calculated. Substituting the value of B and the resistance R at any temp ( $T^\circ\text{A}$ ) in the equation (4)  $\log_{10} A$  can be found and hence A can be calculated

**Voltage current characteristics :** Thermistor, battery and microammeter are connected in series. A voltmeter (0 - 20) is connected across the thermistor. The current is varied gradually and the corresponding current is to be measured. The potential across the thermistor increases with current to certain range, then fall with increases of current. A graph is drawn between voltage and current as show (As the variation is high different meters may have to be used to cover the complete range).





**Observations :**

S.No.	Temperature in °A	$\frac{1}{T}$	Resistance in the arm R while			Resistance of thermistor	$\log_{10} R$
			Heating.	Cooling	Mean		

$$\text{Slope} = \frac{MN}{LM} \dots = 0.4343B$$

$\therefore$  Value of B =

Value of A =

$$\text{Temperature co-efficient of resistance} = \alpha = \frac{R_2 - R_1}{R_1 t_2 - R_2 t_1} = \frac{1}{VR_L}$$

**Viva-Voce Questions**

1. Is the energy gap  $E_g$  of a semiconductor the same at all temperatures ?
2. When will be  $E_g$  maximum ?
3. What do you mean by energy gap ?
4. What is the importance of energy gap ? How will it be for conductor, insulators and semi conductors?
5. Why bands are formed in solids ?

**Viva-Voce Answers**

1. No. the energy gap  $E_g$  decreases with increase of temperatures.
2.  $E_g$  will be maximum at absolute zero temperature.
3. The gap between the energy levels of valence band and conduction band is called the energy gap.
4. The energy gap determines the electrical conducting properties of a material. For conductors  $E_g$  is almost zero, for insulators  $E_g$  -5eV and more, and for semiconductors  $E_g$  -1eV (it varies from 0.2 eV to 2.5 eV).
5. Bands are formed in solids because a large number of atoms are brought close together in a solid. The discrete energy levels of individual atoms, now internal with each other and form bands. Each allowed energy band actually comprises of a large number of closely spaced energy levels.

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**MODEL PAPER - I**  
**B.Sc., Second Year, SEMESTER - III**  
**PHYSICS**  
**(WAVE OPTICS)**

Time : 3 hrs]

[Max. Marks : 75

## Section - A ( 5 x 10 = 50 marks)

Answer any Questions with internal choice from each unit

1. a) Derive an expression for Maxwell's law of distribution of molecular speeds in a gas. (Or)  
 b) What is transport phenomena in a gas? Derive an expression for the coefficient of viscosity of a gas on the basis of kinetic theory.
2. a) Describe the working of Carnot's engine and derive an expression for its efficiency? (Or)  
 b) What is entropy temperature diagram? Obtain expression for the efficiency of a Carnot's engine using the entropy - temperature diagram.
3. a) Derive Maxwell's thermodynamical potentials from thermodynamical laws? (Or)  
 b) Define thermodynamical potentials? Deduce the expression for Clausius - Clapeyron's equation.
4. a) What is Joule-Kelvin effect? Deduce the expression for cooling produced in this effect? (Or)  
 b) Explain the methods producing very low temperature.
5. a) What is black body radiation? Discuss the spectral energy distribution of black body radiation. (Or)  
 b) Define Solar constant? Using Angstrom's pyroheliometer, how we estimate temperature of the sun? Explain.

## Section - B ( 5 x 5 = 25 marks)

Answer any Five of the following questions

6. Derive an expression for diffusion of gases.
7. Describe the experimental method to verify the Maxwell's law of distribution of molecular speeds.
8. Define Reversible and irreversible processes.
9. Deduce the expression for the change of entropy in the universe.
10. Define specific heat of material? Deduce the expression  $C_p - C_v$  for ideal gas?
11. Explain the importance of thermodynamical functions?
12. Write the distinction between Adiabatic and Joule Thomson expansion.
13. Explain the principle of Regenerative cooling?
14. Explain Ferry's black body with neat sketch?
15. Derive Wien's law from Planck's radiation law.

**MODEL PAPER - II**

## Section - A ( 5 x 10 = 50 marks)

Answer any Questions with internal choice from each unit

1. a) Derive an expression for thermal conductivity of a gas on the basis of kinetic theory? (Or)  
 b) Write the postulates of kinetic theory of gases? Describe the toothed wheel experiment to verify the Maxwell's law of distribution of molecular speeds.
2. a) What are isothermal and adiabatic processes? Derive an expressions for work done in these processes? (Or)  
 b) State and prove Carnot's theorem?
3. a) What are thermodynamical potentials? Deduce the Maxwell's equations from thermodynamic potentials? (Or)  
 b) What are thermodynamical potentials? Deduce the expression for Joule - Kelvin coefficient for ideal and van der Waals gas?



4. a) Explain what is meant by Adiabatic demagnetization ? How it is achieved in practical ? Discuss its results?  
(Or)
- b) Describe joule - thomson porous plug experiment. What are the important inferences from this experiment.
5. a) What is planck's hypothesis ? Derive planck's formula for the distribution of energy in black body radiation.  
(Or)
- b) Explain the construction and working of Angstrom's phyro heliometer ? How we estimate using this ?

#### Section - B (5 x 5 = 25 marks)

Answer any Five of the following questions

6. Obtain relation between viscosity and thermal conductivity of gases ?
7. Write a brief note on Mean free path and Degrees of freedom.
8. Write the difference between isothermal and Adiabatic processes.
9. State and explain second law of thermodynamics ?
10. Deduce the expression for ratio of specific heat of material ? ( $C_p - C_v$ )
11. Explain the importance of thermodynamical functions ?
12. Give the properties of substances at low temperatures ?
13. Explain the principle and working of a refrigerator.
14. Discuss Weins black body of radiation.
15. Write a short note on solar constant.

#### MODEL PAPER - III

#### Section - A (5 x 10 = 50 marks)

Answer any Questions with internal choice from each unit

1. a) Explain transport phenomenon of gases ? Derive an expression for diffusion of gases ?  
(Or)
- b) Derive an expression for Maxwell's law of distribution of molecular speeds in a gas ?
2. a) Define entropy ? What is physical concept of entropy write a note on entropy change in reversible and irreversible processes ?  
(Or)
- b) Explain thermodynamic scale of temperature ? Explain how it is perfect to absolute scale.
3. a) Define specific heat of materials ? Deduce the relation between specific heat of materials a)  $C_p - C_v$   
b)  $C_p/C_v$   
(Or)
- b) Deduce the Maxwell's equations from thermodynamic potentials ? Give their significance ?
4. a) What is meant by Adiabatic Demagnetization ? Deduce the expression cooling produced in Adiabatic Demagnetization ?  
(Or)
- b) Discuss Joule - Thomson porous plug experiment ? Discuss the result ?
5. a) Define the basic laws of thermal radiation ?  
(Or)
- b) Derive the expressions for Wein's law and a Rayleigh - Jeans's law from planck's radiation law.

#### Section - B (5 x 5 = 25 marks)

Answer any Five of the following questions

6. Explain transport phenomenon ?
7. Write the postulates of kinetic theory of gases ?
8. State and explain first law of thermodynamics ?
9. Deduce the expression for the change of entropy when Ice changes into steam ?
10. Explain the importance of thermodynamical functions ?
11. Give the applications of clausius - clapeyron equation ?
12. Explain the effects of chlro - fluoro carbons on Ozone layer ?
13. Explain the principle and working of Air conditioning Machine ?
14. What is black body radiation ?
15. Write the postulates of planck's hypothesis ?

