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Department of PHYSICS

II Year B.Sc.-Physics: III Semester
Course-III: HEAT AND THERMODYNAMICS

STUDY MATERIAL

Name of the Student : _____

Roll Number   : _____

Group   : _____

Academic Year   : _____

B.Sc. PHYSICS SYLLABUS UNDER CBCS

For Mathematics Combinations

[2020-21 Batch onwards]

II Year B.Sc.-Physics: III Semester

Course-III: HEAT AND THERMODYNAMICS

UNIT-I: Kinetic Theory of gases: (12 hrs.)

Kinetic Theory of gases-Introduction, Maxwell's law of distribution of molecular velocities (qualitative treatment only) and its experimental verification, Mean free path, Degrees of freedom, Principle of equipartition of energy (Qualitative ideas only), Transport phenomenon in ideal gases: viscosity, Thermal conductivity and diffusion of gases.

UNIT-II: Thermodynamics: (12hrs)

Introduction- Isothermal and Adiabatic processes, Reversible and irreversible processes, Carnot's engine and its efficiency, Carnot's theorem, Thermodynamic scale of temperature and its identity with perfect gas scale, Second law of thermodynamics: Kelvin's and Clausius statements, Principle of refrigeration, Entropy, Physical significance, Change in entropy in reversible and irreversible processes; Entropy and disorder-Entropy of Universe; Temperature-Entropy (T-S) diagram and its uses ; change of entropy when ice changes into steam.

UNIT-III: Thermodynamic Potentials and Maxwell's equations: (12hrs) Thermodynamic potentials-Internal Energy, Enthalpy, Helmholtz Free Energy, Gibb's Free Energy and their significance, Derivation of Maxwell's thermodynamic relations from thermodynamic potentials, Applications to (i) Clausius-Clayperon's equation (ii) Value of CP-CV (iii) Value of CP/CV (iv) Joule-Kelvin coefficient for ideal and Van der Waals' gases

UNIT-IV: Low temperature Physics: (12hrs) Methods for producing very low temperatures, Joule Kelvin effect, Porous plug experiment , Joule expansion, Distinction between adiabatic and Joule Thomson expansion, Expression for Joule Thomson cooling, Liquefaction of air by Linde's method, Production of low temperatures by adiabatic demagnetization (qualitative), Practical applications of substances at low temperatures.

UNIT-V: Quantum theory of radiation: (12 hrs.) Blackbody and its spectral energy distribution of black body radiation, Kirchhoff's law, Wein's displacement law, Stefan-Boltzmann's law and Rayleigh-Jean's law (No derivations), Planck's law of black body radiation-Derivation, Deduction of Wein's law and Rayleigh- Jean's law from Planck's law, Solar constant and its determination using Angstrom pyro heliometer, Estimation of surface temperature of Sun.

Course outcomes

On successful completion of this course, the student will be able to:

- ✓ Understand the basic aspects of kinetic theory of gases, Maxwell-Boltzman distribution law, equipartition of energies, mean free path of molecular collisions and the transport phenomenon in ideal gases

- ✓ Gain knowledge on the basic concepts of thermodynamics, the first and the second law of thermodynamics, the basic principles of refrigeration, the concept of entropy, the thermodynamic potentials and their physical interpretations.

- ✓ Understand the working of Carnot's ideal heat engine, Carnot cycle and its efficiency

- ✓ Develop critical understanding of concept of Thermodynamic potentials, the formulation of Maxwell's equations and its applications.

- ✓ Differentiate between principles and methods to produce low temperature and liquefy air and also understand the practical applications of substances at low temperatures.

- ✓ Examine the nature of black body radiations and the basic theories

UNIT-1
KINETIC THEORY OF GASES

The kinetic theory of gases attempts to explain the microscopic properties of a gas in terms of the motion of its molecules. The gas is assumed to consist of a large number of identical, discrete particles called molecules, a molecule being the smallest unit having the same chemical properties as the substance. Elements of kinetic theory were developed by Maxwell, Boltzmann and Clausius between 1860-1880's. Kinetic theories are available for gas, solid as well as liquids.

FUNDAMENTAL ASSUMPTIONS OF KINETIC THEORY OF GASES: -

1. A gas is composed of a large number of particles called molecules.

2. The molecules are of negligible size compared to the distance between them.

3. In the ideal gas all the molecules are identical, spherical shape and rigid.

4. There is no intermolecular force between the molecules.

5. Collisions take place between the molecules and with the walls of the container producing pressure. These collisions are perfectly elastic collisions.

6. The molecules travel in straight lines between any two successive collisions. The distance travelled by the molecule between two successive collisions is called "free path." The average of all free paths is called mean free path. This is represented by λ**.**

7. $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$ here d= diameter of the molecule, n = No. of molecules per unit volume.

8. The time spent at collision is negligibly small when compared with the time taken by the molecule to travel mean free path.

Average Velocity ($\overline{v}$): -

Average velocity of the molecules in a gas is defined as the mean of the velocities possessed by all the molecules.

Average velocity $\overline{v} = \frac{v_1 + v_2 + v_3 \ldots \ldots + v_n}{n}$

Where $v_1, v_2, v_3 \ldots \ldots v_n$ are the individual velocities and **'n'** is the total number of molecules.

Root mean square Velocity (RMS) $V_{r.m.s}$: -

RMS velocity is defined as the square root of the mean of the squares of the individual velocities.

$$v_{rms} = \sqrt{\frac{v_1{}^2 + v_2{}^2 + v_3{}^2 + \ldots \ldots + v_n{}^2}{n}}$$

Most Probable Velocity V_p: -

Most probable velocity is defined as the velocity with which the largest number of molecules of the gas at a given temperature move.

The relation between the above velocities is $v_{rms} > \bar{v} > v_p.$

MAXWELL'S VELOCITY DISTRIBUTION LAW

According to Maxwell's law of distribution of speeds dn, the number of gas molecules having their speeds between c and $c + dc$ is given by

$$dn = 4\pi n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{\frac{-mc^2}{2kT}} c^2 dc$$

Here n is the total number of molecules per unit volume, m is the mass of each gas molecule, k is Boltzmann constant and T is absolute Temperature.

Maxwell's assumptions of gas molecules: -

1. All the gas molecules in a gaseous system are in random motion having velocity ranges from 0 to ∞.
2. The average density at all points in the gas is same when the gas is in equilibrium condition.
3. Even though the speeds of individual molecules change, a definite number molecules lie in definite range if the temperature remains constant.
4. The probability of a molecule in a particular range depends on the function of velocity and the range of velocity.
5. The velocities of molecules are resolved in to three mutually perpendicular components (u, v, w). They are independent of each other.

Derivation of the equation for velocity distribution function (Maxwell's velocity distribution law): -

Consider a molecule with a velocity 'C' at 'P' vectorialy represented by 'OP' in velocity diagram. It is resolved into components. u, v and w along three mutually perpendicular directions.
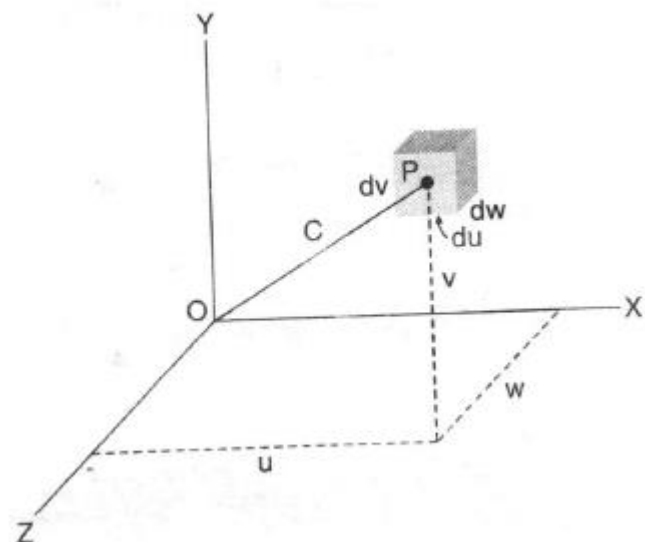
$$C^2 = u^2 + v^2 + w^2 \tag{1}$$

Consider a cube around P with sides du, dv and dw so that, $Volume = du\, dv\, dw$.

The probability that a molecule may have velocity component lying between u and u + du is a function of u and du.

It is represented by f (u) du .Similarly, the probability that a molecule may have velocity component lying between v and v + dv is f(v) dv . The probability that a molecule having velocity component lying between w and w+dw is represented by f (w) dw.

Here the probability of a molecule having velocity components lying between u & u+du, v& v+dv, w & dw is f(u)f(v)f(w) du dv dw.

Let the resultant velocity of molecule is C. The probability that this single velocity C lies in the element of volume du dv dw is **F(C) du dv dw = $\Phi(c^2)$ du dv dw**. Where **Φ** is some function

$f(u)f(v)f(w)dudvdw = \phi(c^2)dudvdw$

$$f(u)f(v)f(w) = \phi(c^2) \tag{1}$$

where $$c^2 = u^2 + v^2 + w^2 \tag{2}$$

For a given velocity $\phi(c^2)$ is a constant => d[$\phi(c^2)$]=0

$$\therefore d[f(u)f(v)f(w)] = 0$$

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

Divide with f(u) f(v) f(w)

$$\frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0 \tag{3}$$

For a given velocity c^2 is also constant,

$$d[c^2] = 0$$

$$=> 2udu + 2vdv + 2wdw = 0$$

$$udu + vdv + wdw = 0 \tag{4}$$

Multiply equation (4) with λ

$$\lambda udv + \lambda vdv + \lambda wdw = 0 \tag{5}$$

where λ is a constant quantity

By adding (3) + (5), we get

$$\left[\frac{f'(u)}{f(u)} + \lambda u\right]du + \left[\frac{f'(v)}{f(v)} + \lambda v\right]dv + \left[\frac{f'(w)}{f(w)} + \lambda w\right]dw = 0$$

Velocity components (u, v, w) are independent of each other.

$$\therefore \left[\frac{f'(u)}{f(u)} + \lambda u\right]du = 0, \left[\frac{f'(v)}{f(v)} + \lambda v\right]dv = 0, \quad \left[\frac{f'(w)}{f(w)} + \lambda w\right]dw = 0 \tag{6}$$

consider $\left[\frac{f'(u)}{f(u)} + \lambda u\right]du = 0$

$$\frac{f'(u)}{f(u)}du + \lambda udu = 0 \Rightarrow \frac{f'(u)}{f(u)}du = -\lambda udu$$

Integrate on both sides

$$log_e[f(u)] = -\lambda \frac{u^2}{2} + log_e a \qquad \Rightarrow log_e\left[\frac{f(u)}{a}\right] = -\lambda \frac{u^2}{2} \qquad \Rightarrow \frac{f(u)}{a} = e^{-\lambda \frac{u^2}{2}}$$

$$f(u) = ae^{-\lambda \frac{u^2}{2}} \Rightarrow f(u) = ae^{-bu^2} \qquad [\because \lambda/2 = b] \tag{7}$$

Similarly

$$f(v) = ae^{-bv^2}$$

$$f(w) = ae^{-bw^2}$$

$$\therefore f(u)f(v)f(w) = a^3 e^{-b(u^2+v^2+w^2)} \tag{8}$$

Where a & b are constants

Let 'n' be the no. of molecules per C.C of the gas. Therefore integrate the above equation by applying boundary conditions

From the definition of probability,

$$n\int\int\int_{-\infty}^{+\infty} f(u)f(v)f(w)\,dudvdw = n$$

$$\int\int\int_{-\infty}^{+\infty} f(u)f(v)f(w)\,dudvdw = 1$$

$$\int\int\int_{-\infty}^{+\infty} a^3 e^{-b(u^2+v^2+w^2)}\,dudvdw = 1 \tag{9}$$

By definite intigral,

$$\int\int\int_{-\infty}^{+\infty} e^{-bu^2}\,du = \sqrt{\frac{\pi}{b}}, Smilarly \quad \int\int\int_{-\infty}^{+\infty} e^{-bv^2}\,dv = \sqrt{\frac{\pi}{b}}, \int\int\int_{-\infty}^{+\infty} e^{-bw^2}\,dw = \sqrt{\frac{\pi}{b}} \tag{10}$$

Thus, $a^3 \sqrt{\frac{\pi}{b}} \sqrt{\frac{\pi}{b}} \sqrt{\frac{\pi}{b}} = 1$

$$a^3 \left(\frac{\pi}{b}\right)^{\frac{3}{2}} = 1$$

$$\therefore a = \left(\frac{b}{\pi}\right)^{\frac{1}{2}}$$

$$But\ b = \frac{m}{2kT} \Rightarrow a = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}$$

Thus, the number 'dn' of molecules having velocity components between u & u+du, v & v+dv, w & dw is

$$dn = n f(u) f(v) f(w)\,dudvdw$$

$$\therefore dn = na^3 e^{-b(u^2+v^2+w^2)}\,dudvdw \tag{11}$$

Substitute a & b values

$$dn = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\left(\frac{-m}{2kT}\right)(u^2+v^2+w^2)}\,dudvdw \tag{12}$$

This is Maxwell's distribution law.

The total number of molecules that lie in a speed of c & c+dc will be obtained by taking the volume element as the space between two concentric spheres of radii c & c+dc drawn from the origin. The volume is

$$\frac{4}{3}\pi[(c+dc)^3 - c^3] = 4\pi c^2 dc \qquad \text{(Neglecting smaller terms (dc}^3\text{, dc}^2\text{))}$$

But $dudvdw = 4\pi c^2 dc$ and $u^2 + v^2 + w^2 = c^2$

$$dn_c = n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\left(\frac{-m}{2kT}\right)^{c^2}} 4\pi c^2 dc$$

$$dn_c = 4\pi n\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mc^2}{2kT}} c^2 dc \qquad \boxed{P(c)dc = \frac{dn_c}{n} = 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\left(\frac{-mc^2}{2kT}\right)} . c^2 dc}$$

This is called as the Maxwell's law of distribution of molecular speeds in a gas.

Graphical representation of Maxwell-Boltzmann's law of distribution of velocities: -

The figure shows the variation of velocity distribution function $P(c)dc = \frac{dn}{n}$ with the speed **v** of molecules at two different temperatures T_1 and T_2 where $T_1 < T_2$
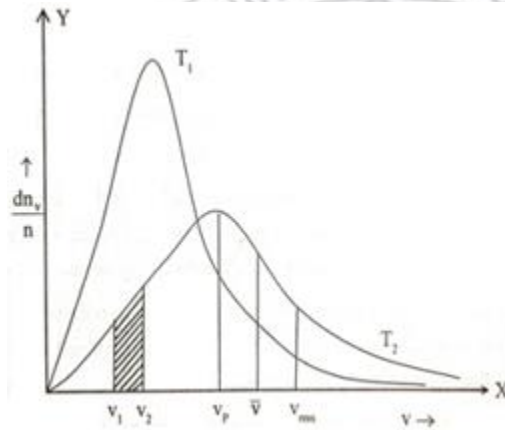

The following points can be noted from the graph.

1. The number of molecules having a speed between v_1 and v_2 equals the area under the curve between the vertical lines at v_1 and v_2.

2. the area under the distribution curve and the
   X- axis is equal to the total number of molecules in the gas.

3. The average speed $\overline{v}$ is somewhat larger than the most probable value.

4. The root mean square value is very larger than the most probable value.

5. As the temperature increases, the $v_{rms}, \overline{v}$ and v_p values increase.

6. The range of typical speeds in grater, so that the distribution curve broadens, as the temperature increases.

7. Since the area under the distribution curve remains the same, the distribution curve flattens as the temperature increases.

EXPERIMENTAL VERIFICATION OF MAXWELL VELOCITY DISTRIBUTION LAW (OR) LAMMERT'S TOOTH HEAD WHEEL METHOD: -
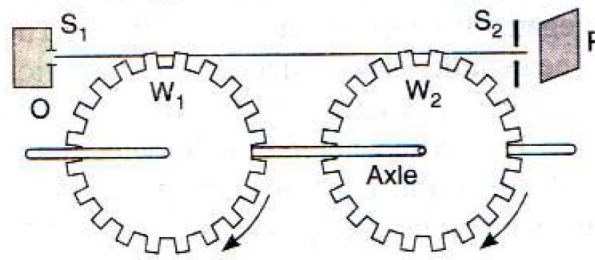
1. This method was used by Lammert in the year 1929.

2. In this method we have two equal toothed wheels W_1 and W_2 with 50 teeth is mounted on the same axel so that they can be rotated together, as shown in the figure.

3. The space between the teeth W_2 is not parallel to those in W_1 but are shifted by 2^0.

4. With the help of the slits S_1 and S_2, a thin and parallel beam of Mercury vapour comes from the oven **'O'**, encounters the slots of W_1 and W_2 successfully and finally passes on to a vertical plate **P**.

5. As the wheels rotate rapidly, the molecular beam that enters W_1 slot does come off fully out through W_2 slot.

6. Only some molecules can pass through the slot in wheel W_2 and are deposit on the plate **P.**

7. The molecules which have required speed to cover the distance W1W2 in a small time interval only pass through a slot in W2. This time must be equal to the time taken by W2 to rotate through 20 .

8. These molecules are deposited on the plate P. Thus the molecules having a particular speed can be separated from the rest by rotating the wheels, the molecules of different speeds are collected at different places on the plate P. Their relative intensities are measured by micro photo meter. From this, the relative no. of molecules lying in different ranges are calculated. A graph is drawn between the intensity (I) and $\dfrac{\bar{c}}{c_p}$ at given temperature this is similar

to the theoritical curve for maxwell's distribution law of molecular speed.
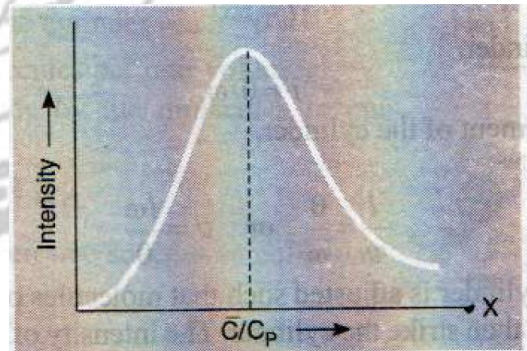
MEAN FREE PATH: -

The distance travelled by a molecule between two successive collisions is called free path. The average distance travelled by molecule between two successive collisions is known as mean free path. If S_1, S_2, ...etc. are distances travelled by a molecule in successive collisions then total distance travelled S $= S_1+ S_2+ S_3+ S_4+....$

If N is the number of Collisions, then mean free path = λ $= \dfrac{S}{N}$

DERIVATION : For the determination of mean free path, it is assumed that only one molecule under consideration is in motion, while all other molecules of the gas are at rest. The molecule under investigation will collide with all those molecules whose centres lie with in a distance 'd' from its centre. Let the molecule is moving with a speed v through the gas. In a time t, the molecule will sweep out a cylinder of length vt and cross sectional area πd^2. This molecule will collide with all the molecules whose centres lie with in the cylinder, whose axis is the line of motion of its centre and radius 'd'.

Volume of the cylinder $= \pi d^2$ vt.

The number of molecules in the cylinder $= \pi d^2$ vtn . Where n is the number of molecules per unit volume.
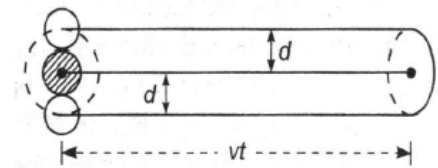
∴ The number of collisions meade by the molecule in one second $= \pi d^2$ vn

Hence average time between two successive collisions $= \dfrac{1}{\pi d^2 vn}$

Average distance between two successive collisions

$= \dfrac{dis\tan ce\ \ cov ered\ \ in\ one\ \sec ond}{No.of\ collisions\ \ made\ \ per\ \sec ond} = \dfrac{v}{\pi d^2\ nv} = \dfrac{1}{\pi d^2\ n}$

∴ Mean free path $= \lambda = \dfrac{1}{\pi d^2 n}$

DEGREE OF FREEDOM

The degrees of freedom of a body is defined as the number of independent motions possible by it or the number of independent coordinates required to specify its dynamic position. It is also the number of independent components of velocities needed to describe the motion of molecules completely. The degrees of freedom of the system is given by

$f = 3\ N - C$

where N is the number of particles in the system and C is the number of independent relations (constraints) among the particles.
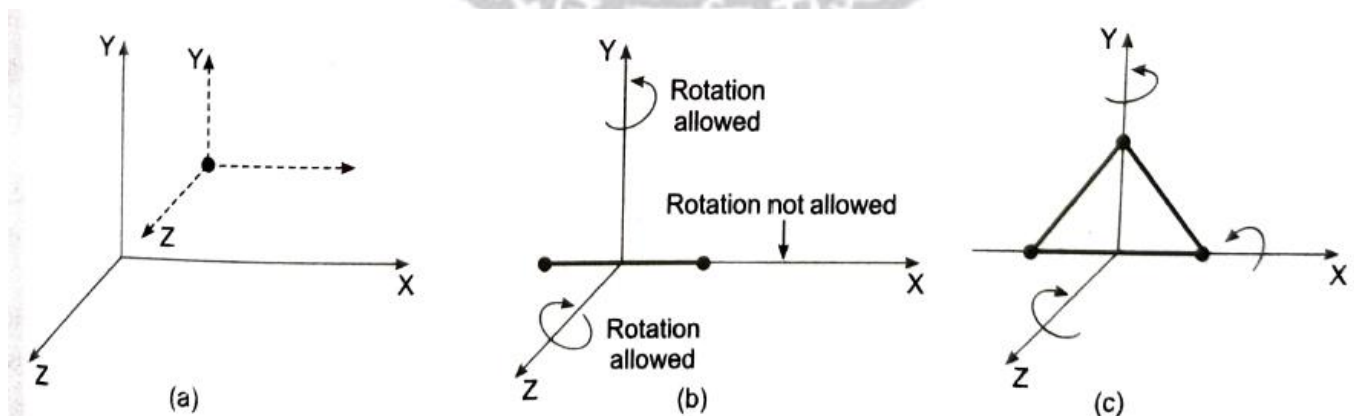
A monoatomic gas (one atom per molecule like neon, argon, helium etc..) has only three translational kinetic energy along the three coordinate axes X, Y and Z. Thus N = 1 and C = 0. f =3. (three degrees of freedom).

A diatomic gas (two atoms per molecule like N_2, O_2. H_2, CO etc….) has both translational and rotational kinetic energies. If there are rotational kinetic energy along two perpendicular axes along with three translational kinetic energy, then N = 2 and C = 1. Thus f = 5.(five degrees of freedom)

A triatomic (three atoms per molecule like, H_2S, H_2O, SO_2) or polyatomic gas there are three translational and three rotational kinetic energies or degrees of freedom for a non-linear molecule. Thus N = 3 and C = 3. This give f = 6. For triatomic linear molecule like CO_2, CS_2, HCN, two atoms lie along the side of the central atom. N = 3, C = 2 and f = 7.

PRINCIPLE OF EQUIPARTITION OF ENERGY

Statement:

According to this law, the total energy of a dynamic system in thermal equilibrium is shared equally by all its degrees of freedom, the energy associated per molecule per degree of freedom being a constant equal to $1/2\ kT$ where k is the Boltzmann constant and T is the absolute temperature of the system.

Proof:

Consider one mole of a monoatomic gas in thermal equilibrium at temperature T. It has three degrees of freedom. According to the Maxwell's theory of equipartition of energy in the steady state, $\overline{u^2} = \overline{v^2} = \overline{w^2}$ where $\bar{u}$, $\bar{v}$ and $\bar{w}$ are the average values of the component velocities of a molecule.

As $c^2 = \overline{u^2} + \overline{v^2} + \overline{w^2}$ Thus $\overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}c^2$

Thus $\frac{1}{2}m\overline{u^2} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{w^2} = \frac{1}{3}\left(\frac{1}{2}mc^2\right)$

According to kinetic theory of gases, the average kinetic energy of a gas molecule is $\frac{1}{2}mc^2 = \frac{3}{2}kT$

Substituting this value in above equation we get,

$$\frac{1}{2}m\overline{u^2} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{w^2} = \frac{1}{3}\left(\frac{3}{2}kT\right)$$

$$= \frac{1}{2}kT$$

Therefore, the average kinetic energy per degree of freedom is equal to $\frac{1}{2}kT$.

The energy associated with the three degrees of freedom is equal to $\frac{3}{2}kT$.

The energy associated with one gram molecule of a gas is given by

$U = N_A \times \frac{3}{2}kT = \frac{3}{2}\left(N_A\ k\right)T = \frac{3}{2}RT$

Thus $U = \frac{3}{2}RT$ where $R = N_A\ k$ and U is the internal energy.

TRANSPORT PHENOMENA: -

Kinetic theory of gases is applied when gas is in equilibrium state. If the gas is not in the equilibrium state then the properties of viscosity, conduction and diffusion arise.

1) The components of the velocity may not have the same value in all parts of the gas. This results in relative motion of the gas layers with respect to each other. As a result fast moving layers transport momentum to the slow moving layers in order to bring the equilibrium state. This gives raise to the phenomenon of viscosity.

2) The different parts of the gas may be at different temperatures. So the gas molecules transport. Kinetic energy (heat energy) from high temperature region to low temperature region in order to bring the equilibrium state. This gives raise to Phenomenon of conduction.

3) The different parts of the gas may have different densities (concentrations) so, the gas molecules transport mass from higher density region to the lower density region in order to bring the equilibrium state. This gives raise to phenomenon of diffusion. The transport of momentum, energy and mass represent viscosity, conduction and diffusion respectively.

     These are known as transport phenomena.

1. VISCOSITY (TRANSPORT OF MOMENTUM): -

Coefficient of viscosity (η) :- It is the tangential force acting per unit area per unit velocity gradient between the layers of a fluid or gas. It is indicated by $'\eta'$.

Tangential force or viscous force $\qquad F \propto A$ and $F \propto -\dfrac{du}{dy}$

$$F = -\eta A \frac{du}{dy}$$

$$\therefore \eta = \frac{F}{(du/dy)} \qquad \text{for unit surface area}$$

Derivation:

Let the gas moving in the positive X- direction on a solid horizontal surface. The flow velocity of gas in contact with surface OX will be zero. The gas may be consider to be consisting of many layers parallel to OX moving under a steady state flow. So it has constant velocity gradient $\dfrac{du}{dy}$ between different layers. Consider a layer AB at distance y from OX and has velocity 'u'. Let us consider two layers CD and EF on either side of AB layer in Y- direction at equal distance of mean free path λ.
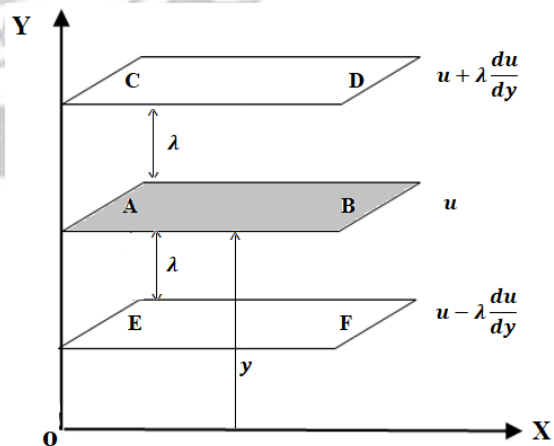
So, the velocity of the gas layer CD is $u + \lambda \left(\dfrac{du}{dy}\right)$

the velocity of the gas layer EF is $u - \lambda \left(\dfrac{du}{dy}\right)$

Let the number of molecules per unit volume be 'n'. From Kinetic theory of gasses, all molecules having random motion in all direction. In that 1/3 of molecules are moving in any of one direction. 1/6th of molecules are moving in upward and downward directions. If 'm' is the mass of the molecule and the average velocity of the gas molecule be $\bar{c}$.

Now the total mass crossing the layer AB in downward or upward direction per unit area per sec is $\dfrac{mn\bar{c}}{6}$.

The momentum carried by the molecules moving downward from CD to AB per unit area per second.

$$p_1 = mass \times velocity = \frac{mn\bar{c}}{6}\left[u + \lambda\left(\frac{du}{dy}\right)\right] \tag{1}$$

The momentum carried by the molecules moving upward from EF to AB per unit area per second

$$p_2 = \frac{mn\bar{c}}{6}\left[u - \lambda\left(\frac{du}{dy}\right)\right] \tag{2}$$

The net momentum carried in downward per unit area per sec is

$$\Delta p = p_1 - p_2$$

$$= \frac{mn\bar{c}}{6}\left[u + \lambda\left(\frac{du}{dy}\right) - u + \lambda\left(\frac{du}{dy}\right)\right]$$

$$= \frac{mn\bar{c}}{6}\left[2\lambda\left(\frac{du}{dy}\right)\right] = \frac{mn\bar{c}}{3}\lambda\left(\frac{du}{dy}\right)$$

This is equal to tangential force between the layers per unit area

So, tangential force $F = \dfrac{mn\bar{c}}{3}\lambda\left(\dfrac{du}{dy}\right)$ $\tag{3}$

The tangential force acting per unit area per unit velocity gradient

$$\eta = \frac{F}{(du/dy)}$$

$$\eta = \frac{\dfrac{mn\bar{c}}{3}\lambda\left(\dfrac{du}{dy}\right)}{(du/dy)}$$

$$\therefore \eta = \frac{1}{3}mn\bar{c}\lambda$$

$$\therefore \eta = \frac{1}{3}\rho\bar{c}\lambda \qquad [\rho = mn] \tag{4}$$

But mean free path, $\lambda = \dfrac{1}{\sqrt{2}\pi d^2 n}$

$$\eta = \frac{1}{3}mn\bar{c}\lambda = \frac{mn\bar{c}}{3} \times \frac{1}{\sqrt{2}\pi d^2 n} = \frac{mn\bar{c}}{3\sqrt{2}\pi d^2 n}$$

$$\eta = \frac{m\bar{c}}{3\sqrt{2}\pi d^2}$$

$$\boxed{\eta = \frac{m\bar{c}}{3\sqrt{2}\pi d^2}} \tag{5}$$

The coefficient of viscosity of gas

1. is directly proportional to mass of the molecule.

2. is directly proportional to average speed of the molecule.

3. is inversely proportional to square of the diameter (d) of the molecule.

2. THERMAL CONDUCTIVITY (TRANSPORT OF ENERGY): -

Coefficient of thermal conduction (K) :-

     Co -efficient of thermal conduction (K) is the amount of heat flowing per unit area per second per unit temperature gradient. It is indicated by $'K'$.

$$\therefore K = \frac{Q}{(dT/dy)}$$

Derivation:

     Let us assume that the gas inside the container divided into several layers, laying the y- axis. Let us assume that layers are at different temperatures and temperature increasing from bottom to top layers with constant temperature gradient $\frac{dT}{dy}$. Consider a layer AB is at temperature 'T' and two other layers CD and EF on either side at a distance of ' λ ' from AB having at temperature $T + \lambda \left(\frac{dT}{dy}\right)$ and $T - \lambda \left(\frac{dT}{dy}\right)$ respectively.

     Let the number of molecules per unit volume be 'n'. Due to temperature difference between gas layers, high temperature molecules transport heat energy to the lower temperature molecules to attain equilibrium. From Kinetic theory of gasses, 1/3 of molecules are moving in any of one direction. 1/6th of molecules are moving in upward and downward directions. If 'm' is the mass of the molecule and the average velocity of the gas molecule be $\bar{c}$. Now the total mass of molecules crossing the layer AB in downward or upward direction per unit area per sec is $\dfrac{mn\bar{c}}{6}$.
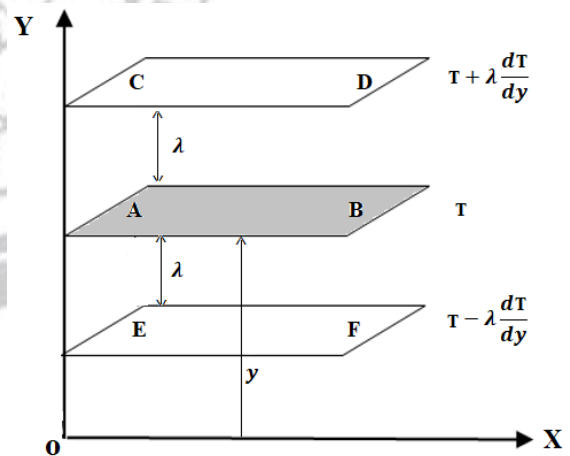
We know that   Heat energy = mass × specific heat × Temperature   (1)

The total heat energy carried by the molecules moving downward from CD to AB per unit area per second

$$Q_1 = \frac{mn\bar{c}}{6} C_v \left[T + \lambda \left(\frac{dT}{dy} \right) \right] \tag{2}$$

The total heat energy carried by the molecules moving upward from EF to AB per unit area per second

$$Q_2 = \frac{mn\bar{c}}{6} C_v \left[T - \lambda \left(\frac{dT}{dy} \right) \right] \tag{3}$$

The net heat energy carried in downward per unit area per sec is

$$Q = Q_1 - Q_2$$

$$= \frac{mn\bar{c}}{6} C_v \left[T + \lambda \left(\frac{dT}{dy} \right) - T + \lambda \left(\frac{dT}{dy} \right) \right]$$

$$= \frac{mn\bar{c}}{6} C_v \left[2\lambda \left(\frac{dT}{dy} \right) \right]$$

$$\therefore Q = \frac{1}{3} mn\bar{c} \ C_v \lambda \left(\frac{dT}{dy} \right) \tag{4}$$

Coefficient of thermal conductivity

$$K = \frac{Q}{\left(dT / dy \right)}$$

$$K = \frac{\frac{1}{3} mn\bar{c} \ C_v \lambda \left(\frac{dT}{dy} \right)}{\left(dT / dy \right)}$$

$$\therefore K = \frac{1}{3} mn\bar{c} \ C_v \lambda$$

$$\therefore K = \frac{1}{3} \rho \bar{c} C_v \lambda \qquad \left[\rho = mn \right] \tag{5}$$

But mean free path, $\lambda = \dfrac{1}{\sqrt{2}\pi d^2 n}$

$$K = \frac{1}{3} mn\bar{c} \ C_v \lambda$$

$$K = \frac{mn\bar{c}C_v}{3} \times \frac{1}{\sqrt{2}\pi d^2 n} = \frac{mn\bar{c}C_v}{3\sqrt{2}\pi d^2 n}$$

$$\therefore K = \frac{m\bar{c} \ C_v}{3\sqrt{2}\pi d^2} \tag{6}$$

Note: The coefficient of thermal conductivity $K = \dfrac{m\bar{c} \ C_v}{3\sqrt{2}\pi d^2} = \eta C_v$

$$\eta = K / C_v \qquad where \ \eta \ \text{is the viscosity of gas} \tag{7}$$

The coefficient of thermal conductivity of a gas

1. is directly proportional to mass of the molecule

2. is directly proportional to average velocity of the molecule

3. is directly proportional to specific heat of the gas at constant volume.

4. is inversely proportional to square of the diameter of the gas molecule.

3. DIFFUSION OF GASES (TRANSPORT OF MASS): -

Consider that the gas is flowing in the positive X-direction. Let us assume the concentration of the gas is not constant at everywhere. $\frac{dn}{dz}$ is the concentration gradient along Z-direction, where **n** is the concentration of molecules in the layer **XY** of figure. There are two layers AB and CD at distance λ on eithersides. Concentration of molecules of Layers
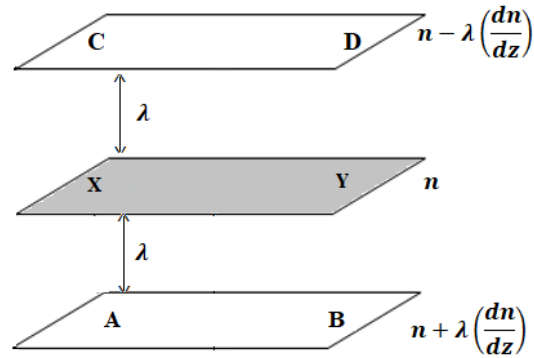
AB and CD are $\left(n + \lambda \frac{dn}{dz}\right)$ and $\left(n - \lambda \frac{dn}{dz}\right)$ respectively.

Due to thermal agitation of molecules, there will be continues interchange of molecules between layers **AB** and **CD**.

The number of molecules crossing through **XY** per unit area and unit time downwards from **CD** to **AB** is

$$\frac{\overline{c}}{6}\left(n + \lambda \frac{dn}{dz}\right)$$

The number of molecules crossing through **XY** per unit area and unit time upwards from **AB** to **CD** is

$$\frac{\overline{c}}{6}\left(n - \lambda \frac{dn}{dz}\right)$$

Net number of molecules passing through the layer XY per unit area per second

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

The coefficient of diffusion D is defined as the ratio of the number of molecules crossing per unit area per second, to the concentration gradient.

$$D = \frac{\frac{1}{3}\overline{c}\lambda \frac{dn}{dz}}{\frac{dn}{dz}}$$

$$\therefore D = \frac{1}{3}\overline{c}\lambda$$

But $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$ and $\overline{C} \propto \sqrt{T}$

$$D = \frac{T^{3/2}}{P}$$

Coefficient of diffusion 'D' is

1) Directly proportional to $T^{\frac{3}{2}}$
2) Inversely proportional to pressure 'P'.

Note: $\eta = \frac{1}{3}mn\overline{c}\lambda = \frac{1}{3}\rho\overline{c}\lambda$ and $K = \frac{1}{3}mn\overline{c}C_v\lambda = \frac{1}{3}\rho\overline{c}C_v\lambda$

So, $\eta = \rho D$ and $K = \rho C_v D$

$\Rightarrow D = \eta / \rho$ and $D = K / \rho C_v$

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UNIT-2

THERMODYNAMICS

</div>

Thermodynamics:

Thermo means heat and dynamic means motion. So thermodynamics means motion by heat. Thermodynamics is a branch of physics which deals with the transformation of thermal (heat) energy into mechanical work or vice- versa.

Heat:

Heat is a form of energy which is transferred from one body to another body due to temperature difference between them.

Unit: Joules, Calories, Ergs. These are also the units for energy

Temperature:

It is a thermal property of substance which measures the relative hotness (or) coldness of a substance.

Unit: C.G.S. ----Celsius(^{0}C)

M.K.S -----Kelvin (K)

Internal Energy (U):

It is defined as the sum of the kinetic energy due to motion of the molecules and potential energy due to molecular force of molecule.

A graph is plotted between pressure and volume is known as indicator diagram. At the point A, P_1 is the pressure and V_1 be the volume. The area under the curve gives the work done by the gas. If the gas is proceed in the reverse direction (from B to A). The area under the curve AB gives the work done on the gas.
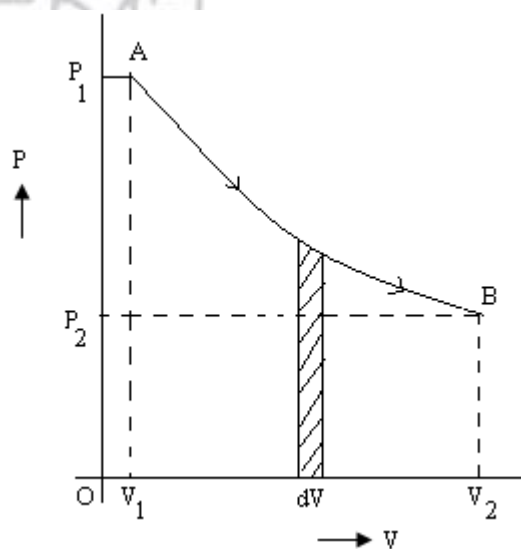
ISOTHERMAL PROCESS:

When a thermodynamic system undergoes a physical change in such a way that its temperature remains constant, then the change is known as isothermal process.

Boyle's law holds good for such a change

PV = Constant

PV = RT

Where R is gas constant per one mole of the gas.

Work done during an Isothermal Process:

The process in which temperature remains constant that process is known as isothermal process. When a gas is allowed to expand isothermally, work is done by it.

Let the initial and final volumes be **V₁** and **V₂** respectively as shown in fig. The work done when the gas expands from **V₁** to **V₂** is given by

$$W = Q = \int_{v_1}^{v_2} P dV$$

$$= \int_{v_1}^{v_2} \frac{RT_1}{V} dV \qquad \left\{ \because P = \frac{RT}{V} \right\}$$

$$= RT_1 \int_{v_1}^{v_2} \frac{1}{V} dV$$

$$W = RT_1 \left[\log V \right]_{v_1}^{v_2} = RT_1 \left[\log V_2 - \log V_1 \right]$$

$$W = RT_1 \log_e \left(\frac{V_2}{V_1} \right) = 2.303 \ RT_1 \log_{10} \left(\frac{V_2}{V_1} \right) \qquad \rightarrow (1)$$

Also $P_1 V_1 = P_2 V_2$ hence $\dfrac{V_2}{V_1} = \dfrac{P_1}{P_2}$

$$\therefore \qquad W = 2.303 \ RT_1 \log_{10} \left(\frac{P_1}{P_2} \right) \qquad \rightarrow (2)$$

Fig. (1)

ADIABATIC CHANGE:

When a thermodynamic system undergoes a change in such way that no exchange of heat takes place between it and the surroundings, the change is known as adiabatic change.

Under this change

1. $PV^{\gamma} = $ Constant   where $\gamma = \dfrac{C_p}{C_V} = $ ratio of two specific heats of a gas

2. $T V^{\gamma-1} = $ Constant

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

Work done during an Adiabatic Process:

The processes in which heat remains constant that processes is called adiabatic processes.

During an adiabatic process, the system is thermally insulated from the surroundings. The gas expands from volume **V₁** to **V₂** as shown in fig (1). The work done when the gas expands from **V₁** to **V₂** is given by

Fig. (2)

$$W = \int_{V_1}^{V_2} PdV = Area \ of \ ABba$$

In Adiabatic Processes $PV^{\gamma} = K$ Constant
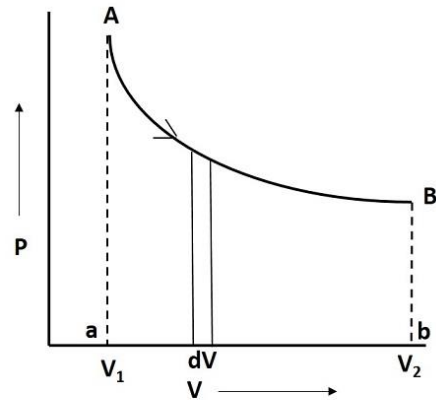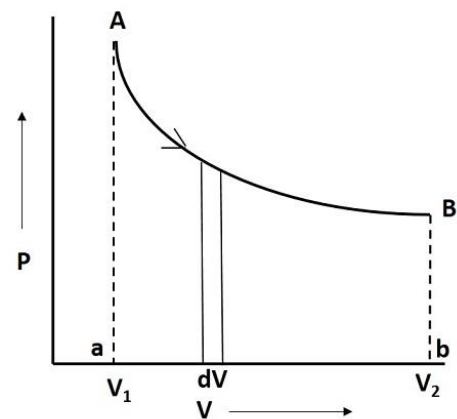
$$W = \int_{V_1}^{V_2} \frac{K}{V^\gamma} dV$$

$$= \int_{V_1}^{V_2} K V^{-\gamma} dV$$

$$= K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2} = \frac{K}{-\gamma+1} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right] = \frac{1}{-\gamma+1} \left[K V_2^{-\gamma+1} - K V_1^{-\gamma+1} \right]$$

In Adiabatic Processes $P_1 V_1^\gamma = P_2 V_2^\gamma = K$ Constant

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

From ideal gas equation $\left[P_2 V_2 = RT_2 \text{ and } P_1 V_1 = RT_1 \right]$

$$= \frac{1}{-\gamma+1} \left[RT_2 - RT_1 \right]$$

$$W = \frac{R}{1-\gamma} \left[T_2 - T_1 \right]$$

The above equation known as work done in an adiabatic process.

Hence the work done in adiabatic process depends only upon the initial and final temperatures T_1 and T_2.

ZEROTH LAW OF THERMODYNAMICS:

If two bodies A and B are in thermal equilibrium with a third body C. They must be in thermal equilibrium with each other.

Thermal equilibrium means that when two bodies are brought into contact with each other and separated by a barrier that is permeable to heat, there will be no transfer of heat from one to the other.
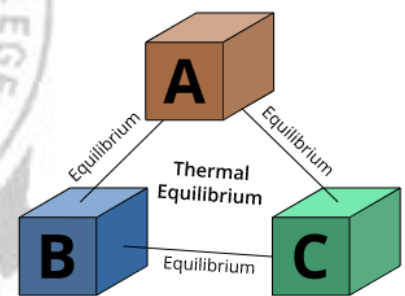
Zeroth law of Thermodynamics

FIRST LAW OF THERMODYNAMICS:

This law gives the principle of conservation of energy. This expresses the equivalence between mechanical work and heat energy. *When a definite amount of work is done, a certain amount of heat is produced and vice versa.*

i.e., W = JH (J=4.2joule/calorie or 4.2 x 10 joule/kilocalorie)

where J is a constant called mechanical equivalent.

This form of the law is true when whole of the work done is used in producing heat or vice versa.

In general, according to first law of thermodynamics, the amount of heat dQ supplied to a system can be utilized as

(i) a part is used in raising the temperature of the system (increasing its internal kinetic energy (dU_k),

(ii) a part is used in doing internal work against molecular attraction (increasing the potential energy of the system (dU_p)

(iii) the rest part is used in doing external work (dW).

$$dQ = dU_k + dU_p + dW$$

$$dQ = dU + dW$$

where dU = increase in total internal energy of the system.

(OR)

It is stated that the sum of increase of internal energy and the work done by the system is equal to the heat given to the system.

$$dQ = dU + dW$$

Significance:

1. The heat is a form of energy.
2. The energy is conserved in thermodynamic system.
3. Every thermodynamic system in equilibrium state possesses internal energy which is a function of the state of the system.

Application:

1. **Isothermal Process:**

    In isothermal process temperature remains constant i.e., $dT = 0$

    $\Rightarrow$ $dU = C_v \, dT = 0$

    First law of thermodynamics $dQ = dU + dW$

    $$dQ = 0 + dW$$

    $$dQ = dW \quad \text{(For Isothermal process)}$$

    The entire energy supplied to the system is utilized to do work only.

2. **Adiabatic process:**

    In adiabatic process $dQ = 0$

    First law of thermodynamics $dQ = dU + dW$

    $$0 = dU + dW$$

    $$dU = -dW \quad \text{(For Adiabatic process)}$$

    The workdone on system is due to expense of the internal energy of the system only.

3. **Cyclic Process:**

    In cyclic process, the change in internal energy and workdone are zero. i.e., $dU = 0, dW = 0$

    $$dQ = 0 \quad \text{(For Cyclic process)}$$

    $$U_f = U_i$$

4. **Isochoric Process:**

    A process takes place at constant volume is known as isochoric process.

    $$dV = 0$$

    We know that $dW = PdV$

    $$dW = 0$$

First law of thermodynamics dQ = dU   (Isochoric Process)

The entire energy supplied to the system is utilized to increase the internal energy of the system only.

5. Isobaric Process:

A process takes place at constant pressure is known as isobaric process. In this process the amount of heat is partly used in increasing the temperature and partly used in External work.

$$dQ = C_p \, dT + P \, dV \qquad \text{(Isobaric process)}$$

REVERSIBLE PROCESS:

A reversible process is one which can be reversed in such a way that all changes occurring in the direct process are exactly repeated in the opposite direction.

If heat is absorbed in the direct process, the same amount of heat should be given out in the reverse process. If work is done on the gas in direct process then the same amount of work is done by the gas in reverse order.

Conditions:

1. In this the dissipative forces like friction, viscosity etc, must be absent

2. It is infinitely slow process.

3. The temperature of the system must not differ from the surroundings.

Ex:

1. All isothermal and adiabatic changes, if they are performed very slowly.

2. When a certain amount of heat is absorbed by ice it melts. If same amount of heat is removed from it, the water formed on the direct process will be converted into ice.

3. Very slow evaporation or condensation.

IRREVERSIBLE PROCESS:

Any process which is not reversible exactly is an irreversible process, all natural processes such as conduction, radiation, friction, radioactive are irreversible.

Ex:

1. When heat produced by the flow of current through resistance.

2. Heat transfer between bodies at different temperatures.

3. Joule Thomson expansion.

Difference between Reversible and Irreversible processes

Reversible Processes	Irreversible Processes
1. In this processes the system is brought to the initial state without any change where in the surroundings.	1. In this processes the system is brought to the initial state only at the cost of some change in the surroundings.
2. The change in internal energy is zero i.e., dU = 0	2. The change in internal energy is zero i.e., dU ≠ 0
3. The network flow is zero i.e., dW = 0	3. The network flow is zero i.e., dW ≠ 0

4. The net heat flow is zero. i.e., dQ = 0	4. The net heat flow is zero. i.e., dQ ≠ 0
5. This processes occurs slowly.	5. This processes occurs rapidly, spontaneously
6. This is an ideal concept	6. This is the most practical one.
7. This must be free from dissipative forces like friction, viscosity etc	7. This process takes place only when there is some dissipative force

CARNOT'S ENGINE (OR) REVERSIBLE ENGINE

A heat engine is a device to convert heat into work. In 1824 Carnot considered a theoretical engine which is free from all the practical imperfections. Such an engine cannot be realized in practice. It has maximum efficiency and it is an ideal heat engine. The engine is shown in the figure. It consists of the following parts:
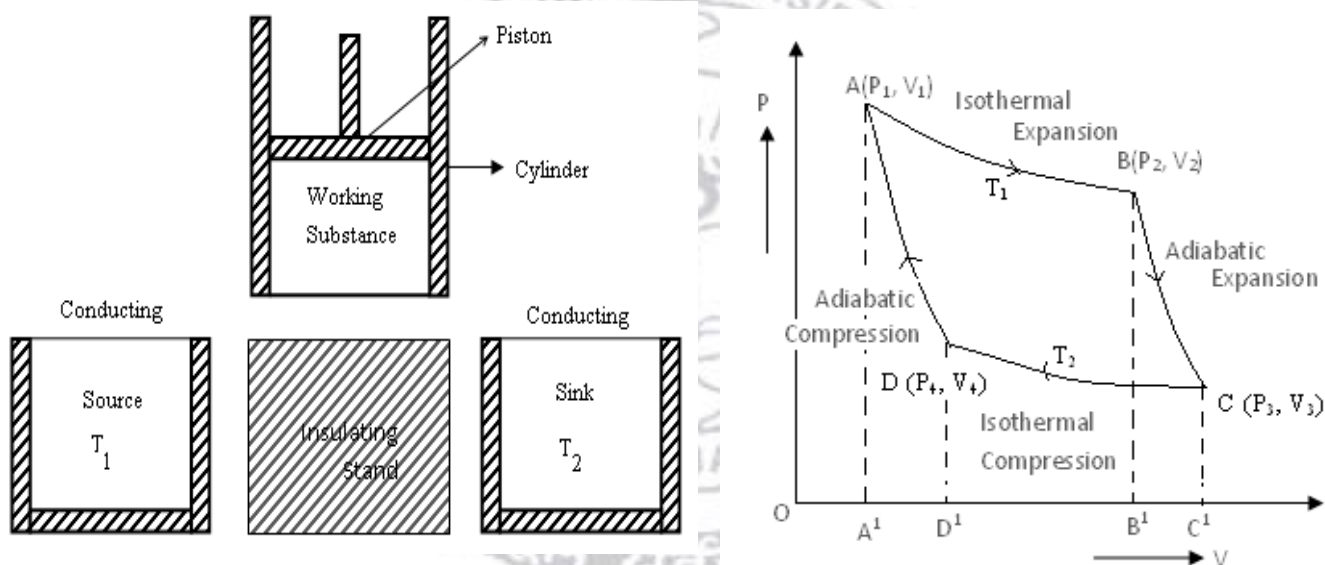
1. **Working Substance:** The working substance is an ideal gas enclosed in a cylinder-piston arrangement. The cylinder is made with non-conducting walls and conducting base. The non-conducting piston moves without friction.
2. **The Source:** A hot body high thermal capacity maintained at a high temperature T_1 K serves as a source.
3. **Sink:** A cold body maintained at a lower temperature T_2 K serves as a sink.
4. **Insulating Stand:** To make the whole system perfectly a non-conducting stand is put on the base of the cylinder.

CARNOT'S CYCLE:

The working substance is made to undergo a cyclic operation made up of 4 parts as shown in the above figure.

I. Isothermal expansion, II. Adiabatic expansion, III. Isothermal compression and IV. Adiabatic compression

Isothermal Expansion AB:

Consider that one gram mole of a gas is contained in the cylinder. Let initial state of the gas is denoted by "A" on the indicator diagram. When the temperature T_1, pressure P_1 and volume V_1, the cylinder is placed on the source and the piston is moved slowly upwards so that the gas expands isothermally. In this operation, the pressure of the gas falls and the volume increases. The final state of a gas is represented by "B". Thus the isothermal expansion is represented by the curve AB on the indicator diagram. Let Q_1 be the quantity of heat absorbed by the gas from the source. This is equal to the amount of work 'W_1' done by the gas. During this expansion, work done by the gas

$$W_1 = Q_1 = \int_{v_1}^{v_2} P dv = \int_{v_1}^{v_2} \frac{RT_1}{V} dv \qquad \left\{ \because P = \frac{RT}{V} \right\}$$

$$W_1 = RT_1 \int_{v_1}^{v_2} \frac{1}{V} dv = RT_1 \left[\log V \right]_{v_1}^{v_2} = RT_1 \left[\log V_2 - \log V_1 \right]$$

$$W_1 = RT_1 \log_e \left(\frac{V_2}{V_1} \right) = 2.303 \, RT_1 \log_{10} \left(\frac{V_2}{V_1} \right) = area \ of \ ABB'A'A \qquad \rightarrow (1)$$

Adiabatic Expansion BC:

The cylinder is removed from the source and is placed on insulating stand. The piston is allowed to move further adiabatically till the temperature of the gas is same as that of the sink ($T_2 {}^\circ$K). Hence, the gas done an external work at the expense of internal energy. This expansion is represented by the curve BC on the indicator diagram.

Work done by the gas,

$$W_2 = \int_{v_2}^{v_3} P dv = \int_{v_2}^{v_3} \frac{k}{V^\gamma} dv \qquad \{PV^\gamma = K\}$$

$$W_2 = K \int_{v_2}^{v_3} v^{-\gamma} dv = K \left[\frac{v^{-\gamma+1}}{-\gamma+1} \right]_{v_2}^{v_3} = \frac{K}{-\gamma+1} \left[v^{-\gamma+1} \right]_{v_2}^{v_3}$$

$$W_2 = \frac{K}{1-\gamma} \left[v_3^{1-\gamma} - v_2^{1-\gamma} \right] = \frac{1}{1-\gamma} \left[Kv_3^{1-\gamma} - Kv_2^{1-\gamma} \right]$$

In Adiabatic Processes $P_2 V_2{}^\gamma = P_3 V_3{}^\gamma = K$ Constant this value is substituting in above equation, then we get

$$W_2 = \frac{1}{1-\gamma} \left[p_3 v_3^\gamma v_3^{1-\gamma} - p_2 v_2^\gamma v_2^{1-\gamma} \right]$$

$$W_2 = \frac{1}{1-\gamma} \left[p_3 v_3 - p_2 v_2 \right] = \frac{1}{1-\gamma} \left[RT_2 - RT_1 \right]$$

$$W_2 = \frac{R}{1-\gamma} \left[T_2 - T_1 \right] = area \ of \ BCC'B'B \qquad \rightarrow (2)$$

Isothermal Compression CD:

The cylinder is remove from the insulating stand and placed on the sink at $T_2{}^\circ K$. The piston is compressed very slowly till the gas attains the state D whose co-ordinates are (P_4, V_4). Here the heat of compression so developed passes to the sink. The operation is shown by the curve CD. Let Q_2 be the quantity of heat rejected to the sink and equal to the amount of work done on the gas.

$$W_3 = \int_{v_3}^{v_4} P dv = \int_{v_3}^{v_4} \frac{RT_2}{V} dv = RT_2 \int_{v_3}^{v_4} \frac{1}{V} dv$$

$$W_3 = RT_2 \left[\log V\right]_{v_3}^{v_4} = RT_2 \log_e \left[\frac{v_4}{v_3}\right] = -RT_2 \log_e \left[\frac{v_3}{v_4}\right]$$

$$W_3 = Q_2 = -2.303 RT_1 \log_{10} \left(\frac{v_3}{v_4}\right) = area\ of\ CDD'C'C \rightarrow (3)$$

Adiabatic Compression DA:

The cylinder is detached from the sink and placed on the stand. The gas is compressed such that it undergoes an adiabatic compression till the state A is again reached. Now the temperature raises from $T_2{}^\circ K$ to $T_1{}^\circ K$. This operation is represented by the curve DA on the indicator diagram.

Work done on the gas,

$$W_4 = \int_{v_4}^{v_1} P dv = \int_{v_4}^{v_1} \frac{K}{v^\gamma} dv = K \int_{v_4}^{v_1} \frac{1}{v^\gamma} dv$$

$$W_4 = K \left[\frac{v^{-\gamma+1}}{-\gamma+1}\right]_{v_4}^{v_1} = \frac{K}{1-\gamma} \left[v_1^{1-\gamma} - v_4^{1-\gamma}\right]$$

$$W_4 = \frac{1}{1-\gamma} \left[K v_1^{1-\gamma} - K v_4^{1-\gamma}\right] = \frac{1}{1-\gamma} \left[p_1 v_1^\gamma v_1^{1-\gamma} - p_4 v_4^\gamma v_4^{1-\gamma}\right] [\because K = pv^\gamma]$$

$$W_4 = \frac{1}{1-\gamma} \left[p_1 v_1 - p_4 v_4\right] = \frac{1}{1-\gamma} \left[RT_1 - RT_2\right]$$

$$\boldsymbol{W_4 = \frac{R}{1-\gamma} \left[T_1 - T_2\right] = area\ of\ DAA'D'D} \text{ -------- (4)}$$

Total work done by the engine,

$$W = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \log_e \left(\frac{v_2}{v_1}\right) + \frac{R}{1-\gamma} \left[T_2 - T_1\right] - RT_2 \log_e \left[\frac{v_3}{v_4}\right] + \frac{R}{1-\gamma} \left[T_1 - T_2\right]$$

$$= RT_1 \log_e \left(\frac{v_2}{v_1}\right) - \frac{R}{1-\gamma} \left[T_1 - T_2\right] - RT_2 \log_e \left[\frac{v_3}{v_4}\right] + \frac{R}{1-\gamma} \left[T_1 - T_2\right]$$

$$= RT_1 \log_e \left(\frac{v_2}{v_1}\right) - RT_2 \log_e \left[\frac{v_3}{v_4}\right]$$

$$W = R \left[T_1 \log_e \left(\frac{v_2}{v_1}\right) - T_2 \log_e \left[\frac{v_3}{v_4}\right]\right] \text{------- (5)}$$

The points A and D lie on the same adiabatic DA then

$$\boldsymbol{T_1 V_1{}^{\gamma-1} = T_2 V_4{}^{\gamma-1}}$$

$$\frac{T_2}{T_1} = \frac{V_1^{\gamma-1}}{V_4^{\gamma-1}} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \text{-------- (6)}$$

The points B and C lie on the same adiabatic BC, then

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \frac{V_2^{\gamma-1}}{V_3^{\gamma-1}} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \text{-------- (7)}$$

From equation (6) and (7)

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \Rightarrow \left(\frac{V_1}{V_4}\right) = \left(\frac{V_2}{V_3}\right)$$

$$\Rightarrow \left(\frac{V_3}{V_4}\right) = \left(\frac{V_2}{V_1}\right) \qquad \text{--------- (8)}$$

Equation (8) is substituting in equation (5) then we get

$$W = R\left[T_1 \log_e \frac{V_2}{V_1} - T_2 \log_e \frac{V_2}{V_1}\right]$$

$$W = R(T_1 - T_2)\left[\log_e \frac{V_2}{V_1}\right] \text{-------- (9)}$$

Efficiency(η):

Efficiency $\eta = \dfrac{\text{Work done by the engine}}{\text{Heat taken from the source}} = \dfrac{W}{Q_1} = \dfrac{Q_1 - Q_2}{Q_1}$

$$\eta = 1 - \frac{Q_2}{Q_1} \qquad \text{(or)}$$

$$\eta = \frac{\text{Heat converted into work}}{\text{Heat taken}} = \frac{R\left[T_1 - T_2\right]\log_e\left(\dfrac{v_2}{v_1}\right)}{RT_1 \log_e\left(\dfrac{v_2}{v_1}\right)}$$

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

The efficiency depends only upon the temperatures of the source and sink and is always less than unity (1). The efficiency is independent of the nature of the working substance.

SECOND LAW OF THERMODYNAMICS:

KELVIN'S STATEMENT:

We know that a heat engine takes heat from the source, converts a part of it into mechanical work and the balance is rejected to the sink. As the engine absorbs more and more and more heat from the source, its temperature falls and after some time its temperature becomes as that of surroundings.

Now, no heat flow will be possible in this case, the engine stops working. This consideration led Kelvin to state the second law as,

"It is impossible to derive a continuous supply of work by cooling a body to a temperature lower that of its surroundings."

CLAUSIUS STATEMENT:

The Clausius statement of second law is based on the working of refrigerator. In refrigerator, the transfer of heat takes place from a cold body to hot body with the aid of an external agency. This consideration led to Clausius second law as

"It is impossible for a self-acting machine unaided by any external agency to transfer heat from a cold body to a hot body".

CARNOT THEOREM

Statement: No heat in a can be more efficient then reversible engine working between the same two temperatures. (OR) All reversible engines working b / w the same two temperatures have same efficiency whatever may be the working substance.

Proof:-

Consider a reversible engine (R) and Irreversible engine (I) working with the same source and sink. I works in the forward direction and R works in the backward direction. Let I absorb an energy 'Q' from source and convert a part of it into work (W) and transfer (Q-W) to the sink. Similarly R absorbs energy Q' from the sink, a certain amount of

work (W') is done on that working substance and transfer ($Q' + W'$) amount to the source.
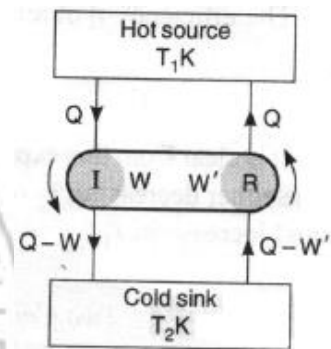
Here we assume that the source is left with no change.

Hence $Q' + W' = Q$ $W' = Q - Q'$

Efficiency of I is $(\eta_I) = \dfrac{W}{Q}$ and Efficiency of R is $\eta_R = \dfrac{W'}{Q}$

let, $\eta_I > \eta_R$

$\Rightarrow \quad \dfrac{W}{Q} > \dfrac{W'}{Q}$

$\Rightarrow \quad W > W'$

When the two engines are coupled the net amount of heat drawn from the sink is (Q- W')-(Q-W). This is positive. This shows that (Q- W') > (Q-W), which is impossible according to the second law of Thermodynamics. Hence irreversible engine cannot be more efficient than reversible engine.

To prove the II part of the theorem, consider two reversible engines A and B working between the same source and sink. If A drives B in back ward direction then A cannot be more efficient than B and vice - versa. So, both are equally efficient. So, the efficiency of the reversible engine depends on the temperatures of source and sink and independent of the nature of the working substance.

Coefficient of performance:

Coefficient of performance K is defined as the ratio of heat taken to form the cold body to the work needed to run the refrigerator.

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

The good refrigerator should have a high efficient of performance.

Relation between efficiency of Carnot's engine and the coefficient of performance of Carnot's refrigerator:

We know that $\eta = \frac{T_1 - T_2}{T_1}$ and $K = \frac{T_2}{T_1 - T_2}$

$$K + 1 = \frac{T_2}{T_1 - T_2} + 1$$

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

$$K + 1 = \frac{1}{\eta} \text{ or } \eta = \frac{1}{K + 1}$$

Kelvin's Scale of Temperature (or) Thermodynamic Scale of Temperature (or) Absolute Scale of Temperature:

In the year 1848 Kelvin started with the Carnot engine to the basics of temperature measurements. He started with the result that efficiency of all reversible engine working between the same two temperatures is a function of those two temperatures and is independent of nature of the working substance. This forms the basis of Kelvin scale. The Kelvin scale is also called the thermodynamic scale.

Let Q_1 be the amount of heat absorbed by a Carnot reversible engine at a higher temperature T_1 and Q_2 be the quantity of heat rejected at a lower temperature T_2. The efficiency of Carnot engine is a function of two temperatures only and we can write,

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

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

$$= f(T_1, T_2)$$

$$1 - \frac{Q_2}{Q_1} = f(T_1, T_2) \Rightarrow 1 - f(T_1, T_2) = \frac{Q_2}{Q_1}$$

$$\frac{Q_1}{Q_2} = \frac{1}{1 - f(T_1, T_2)} = F(T_1, T_2) \qquad\qquad \rightarrow (1)$$

If we consider a 2nd Carnot engine absorbing heat Q_2 at temperature T_2 and rejecting heat Q_3 at temperature T_3. Then

$$\frac{Q_2}{Q_3} = F(T_2, T_3) \qquad\qquad \rightarrow (2)$$

Now let us consider a 3rd Carnot engine absorbing heat Q_1 at temperature T_1 and rejecting heat Q_3 at temperature T_3. Then

$$\frac{Q_1}{Q_3} = F(T_1, T_3) \qquad\qquad \rightarrow (3)$$

From (1) & (2)

$$\frac{Q_1}{Q_2}.\frac{Q_2}{Q_3} = F(T_1, T_2).F(T_2, T_3)$$

$$\frac{Q_1}{Q_3} = F(T_1, T_2).F(T_2, T_3)$$

From (3)

$$F(T_1, T_3) = F(T_1, T_2).F(T_2, T_3) \qquad\qquad \rightarrow (4)$$

Such kind of relation as (4) will be possible only when $F(T_1, T_2) = \dfrac{\phi(T_1)}{\phi(T_2)}$

$$F(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$$

$$F(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)}$$

Here ϕ is function of temperature

$$\therefore \frac{Q_1}{Q_2} = \frac{\phi(T_1)}{\phi(T_2)} = \frac{\tau_1}{\tau_2}(\text{say})$$

Where τ_1 and τ_2 are the temperatures.

$$\Rightarrow \frac{Q_1}{Q_2} = \frac{\text{Quantity of heat transferred at } \tau_1}{\text{Quantity of heat transferred at } \tau_2}$$

Thus the thermodynamic scale of temperature is that scale to which the ratio of any two temperatures is the same as the ratio of heat transferred by a Carnot reversible engine operating between these two temperatures.

Absolute Zero:

The efficiency of Carnot engine

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{\phi(T_2)}{\phi(T_1)} = 1 - \frac{\theta_2}{\theta_1}$$

When $\tau_2 = 0$ then $\eta = 1$

Thus the zero of the absolute scale is defined as the temperature of the sink for a reversible engine which converts all the heat into work and has efficiency equal to one. This zero is called the absolute zero.

Negative temperature:

If the temperature is less than absolute zero then the efficiency of the reversible engine must be more than 1 (or 100%) which is impossible according to second law of thermodynamics. So negative temperature on Kelvin scale of temperature is not possible.

ENTROPY (S):

Entropy is the thermal property of a body remains constant during a reversible adiabatic process. It is also known as ''Thermal Intertia''. The measurement of absolute value of entropy is not possible. Hence we can measure only change in entropy. Entropy is also a measure of randomness or disorder of molecules of a system. If dQ be infinitesimal amount of heat taken (or) rejected at temperature T_1, the change in entropy is

$$dS = \frac{dQ}{T}$$

Explanation: - Consider a number of isothermals at temperatures T_1, T_2, T_3, etc and adiabatics A & B. The adiabatics cut the isothermals at a,b,c,d,e & f.

Consider a reversible carnot cycle abcda for the working substance between the temperatures T_1 & T_2 Suppose Q_1 amount of heat is taken at T_1 and Q_2 amount of heat is rejected at T_2

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \text{ or } \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \qquad (1)$$

similarly if we consider the carnot cycle cdefc we get

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \qquad (2)$$

from (1) & (2)

We can Write

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = ...$$

In general we can write $\frac{Q}{T}$ = constant

The constant $\frac{Q}{T}$ is known as entropy. The measurement of absolute entropy is not possible we can measure only change of entropy (dS) as the substance moves from one state to another state.

Change of entropy $(dS) = \dfrac{Heat\ energy\ dQ}{Temperature\ T}$

Now we can write. $dQ = TdS$ (3)

This represents mathematical form of second law of Thermodynamics.

Physical significance:- The entropy of a substance is a real physical quantity and is a definite function of the state of a body like pressure, temperature, internal energy etc.

By definition,

$$change\ of\ entropy = \frac{heat\ energy}{temperature}$$

$$change\ of\ entropy \times temperature = heat\ energy$$

If we compare the above equation with PE = mgh, height is equal to temperature and entropy corresponds to mass (or) Inertia (or) Thermal Interia.

Hence entropy may be thought of as a quantity which bears to heat motion a similar relation as mass bears to linear motion and moment of inertia in rotational motion.

If entropy of a system increases the system goes from order to disorder state
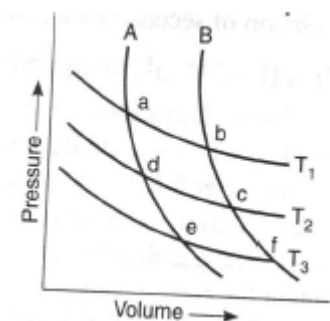
CHANGE IN ENTROPY IN A REVERSIBLE CYCLE OR PROCESS:

Consider a reversible Carnot cycle as shown in the figure.

From A to B the working substance absorbs a quantity of heat Q_1 at T_1 during isothermal expansion. Increase in entropy of the working substance $= \dfrac{Q_1}{T_1}$

During the adiabatic expansion BC no heat is taken out (or) taken in by the working substance and so there is no change in entropy.

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

Decrease in entropy of the working substance $= \dfrac{Q_2}{T_2}$

During the adiabatic compression DA again there is no change in entropy.

Net change in entropy of the working substance in the cycle ABCDA $= \dfrac{Q_1}{T_1} - \dfrac{Q_2}{T_2}$

But $\dfrac{Q_1}{T_1} = \dfrac{Q_2}{T_2}$ $\left(\because \text{By Kelvin seale of temperature} \right)$

$\therefore$ Net change $= 0$

Hence total change in entropy of the working substance in a reversible process is Zero. This statement is also known as Clausius theorem.

CHANGE IN ENTROPY IN AN IRREVERSIBLE PROCESS:

During an irreversible process like conduction, radiation heat is lost by a hot body at higher temperature T_1 and heat is gained by a cold body at lower temperature T_2. Let Q_1 be the quantity of heat given out by the hot body at temperature T_1 and the quantity of heat Q_2 gained by the cold body at temperature T_2.

Consider the hot body and cold body as one system. Decrease in entropy of hot body $= \dfrac{Q_1}{T_1}$
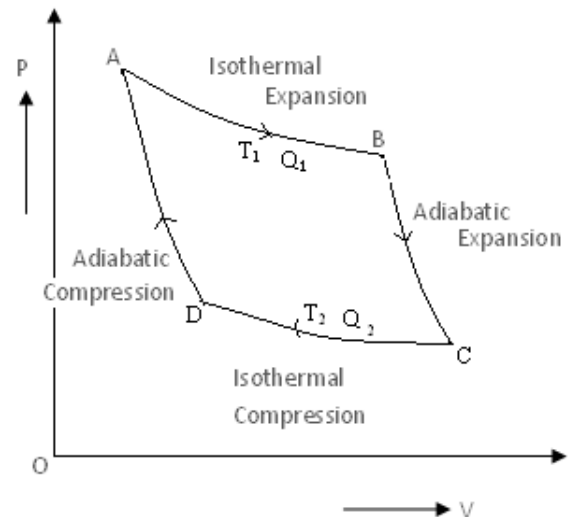
Increase in entropy of cold body $= \dfrac{Q_2}{T_2}$

The net change in entropy of the system, $\dfrac{Q_2}{T_2} - \dfrac{Q_1}{T_1}$

It is a positive quantity, since $T_2 < T_1$

$\therefore \dfrac{Q_2}{T_2} > \dfrac{Q_1}{T_1}$

Thus the entropy of the system increases in an irreversible process.

ENTROPY AND DISORDER

Entropy is a measure of degree of disorder. When a substance changes from solid to liquid (or) liquid to gas disorderliness increases so entropy increases similarly when a substance changes from gas to liquid (or) liquid to solid disorder decreases. So, entropy decreases.

Ex:- Free expansion, Heat conduction.

Free expansion: - Consider two vessels A & B are connected with stop cock. A is filled with gas and B is vacuumed. When stop cock is suddenly opened the gas molecules spread into B and have random nature.

So, expansion takes place.

∴ Entropy and disorder increase.

Heat conduction: - When two bodies which are at different temperatures ($T_2 > T_1$) are put in contact then heat flows from the hot body to cold body until both attain common temp. As a result, disorder increases due to expansion. So, entropy also increases.

ENTROPY OF UNIVERSE

The entropy of universe changes due to irreversible process but not with the reversible process. But in universe all processes are irreversible So, entropy of universe is increasing. When an irreversible process takes place the available energy converts into work. So, the available energy decreases. This is called principle of degradation. The Principle of degradation states that the available energy of the universe is tending to 0. Consider a Carnot engine. In this Q_1 amount of heat is taken at temperature T_1 and Q_2 amount of heat is given out at temperature T_2. The quantity of heat ($Q_1 - Q_2$) is converted into work and known as available energy.

$$\text{Available energy } Q_1 - Q_2 = Q_1\left(1 - \frac{Q_2}{Q_1}\right) = Q_1\left(1 - \frac{T_2}{T_1}\right)$$

let, $T_2 = T_0$ be the lowest available temperature. Consider the heat conduction from a body at T_1 K to body a T_2 K. Let Q be the amount of heat flowing from a point at high temperature to a point at low temperature.

$$\text{Available energy before transfer} = Q\left(1 - \frac{T_0}{T_1}\right)$$

$$\text{Available energy after transfer} = Q\left(1 - \frac{T_0}{T_2}\right)$$

$$\text{Loss of available energy} = Q\left(1 - \frac{T_0}{T_1}\right) - Q\left(1 - \frac{T_0}{T_2}\right) = Q\left(\frac{T_0}{T_2} - \frac{T_0}{T_1}\right) = T_0\left(\frac{Q}{T_2} - \frac{Q}{T_1}\right)$$

$$= T_0 \, dS$$

The above equation indicates that the entropy is increasing while available energy is decreasing. As irreversible processes are continuously going on in nature, the entropy of universe is increasing.

THE CHANGE OF ENTROPY WHEN ICE CONVERTS INTO STEAM

Let m grams of ice at T_1 K converts into steam at T_2 K. Let L_1 and L_2 be the Latent heats of fusion and vaporization respectively. First of all, m grams of ice at T_1 K converts into water when heat is supplied.

Change in entropy (ds_1) $= \dfrac{mL_1}{T_1}$ (1)

When the temperature of the water changes from T_1 K to T_2 K.

Change of entropy (ds_2) $= \int_{T_1}^{T_2} \dfrac{dQ}{T} = mC \int_{T_1}^{T_2} \dfrac{dT}{T}$

$= mC \log_e \left(\dfrac{T_2}{T_1} \right)$, where C is the specific heat of water

$= 2.303 mC \log_{10} \left(\dfrac{T_2}{T_1} \right)$ (2)

finally, the water converts into steam at T_2K.

∴change of entropy (ds_3) $= \dfrac{mL_2}{T_2}$ (3)

∴The total change of entropy (ds) when ice convers into steam is given by $ds = ds_1 + ds_2 + ds_3$

(ds) $= \dfrac{mL_1}{T_1} + 2.303 mC \log_{10} \left(\dfrac{T_2}{T_1} \right) + \dfrac{mL_2}{T_2}$

TEMPERATURE- ENTROPY DIAGRAM: (T-S DIAGRAM) OR (TEPHIGRAM):

A graph is plotted in temperature and entropy is known as temperature-entropy diagram. Consider a Carnot's cycle. Hence the working substance undergoes isothermal expansion, adiabatic expansion, Isothermal compression and adiabatic compression operations.
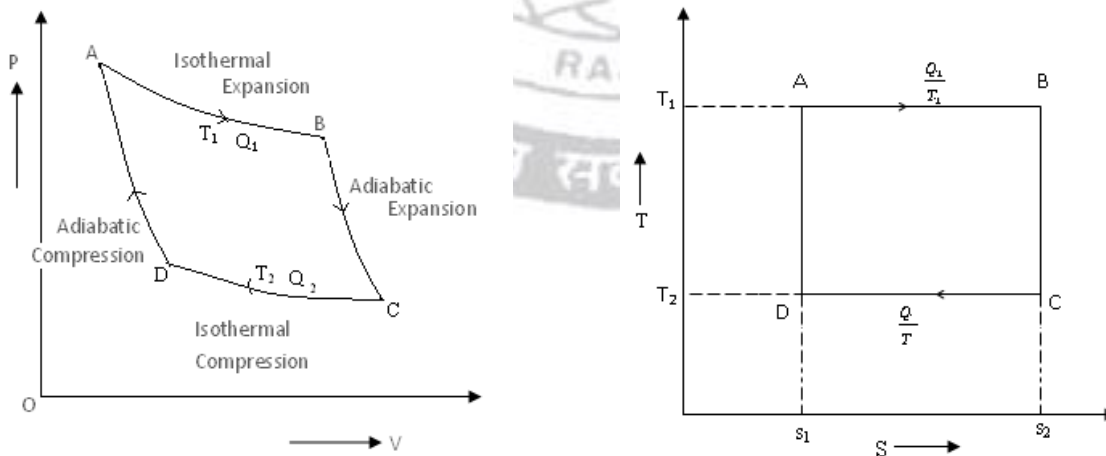
In the isothermal expansion in Carnot cycle absorbs an amount of heat Q_1 at T_1° K. Hence the entropy of the substance increases $\dfrac{Q_1}{T_1}$. It is represented by AB on the Tephigram.

During the adiabatic expansion the entropy remains constant. So this case is represented by BC on the Tephigram.

During the isothermal compression the working substance rejects at T_2° K, so its entropy decreases by $\dfrac{Q_2}{T_2}$. This is represented by CD on the Tephigram.

During the adiabatic compression the entropy remains constant. This is represented by DA on Tephigram.

Thus ABCD rectangle represents the Carnot cycle.

The amount of heat $Q_1 = T_1(S_2-S_1)$

$$= \text{area } ABS_2S_1A$$

Amount of heat Q_2 rejected to the sink, $Q_2 = T_2(S_2-S_1)$

$$= \text{area } BCS_1S_2D$$

Thus,

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{Area\,of ABCDA}{Area\,of\ ABS_1S_2A}$$

$$= \frac{T_1\left(S_2 - S_1\right) - T_2\left(S_2 - S_1\right)}{T_1\left(S_2 - S_1\right)}$$

$$= \frac{\left(T_1 - T_2\right)\left(S_2 - S_1\right)}{T_1\left(S_2 - S_1\right)} = \frac{T_1 - T_2}{T_1}$$

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

USES:
1. They are used in meteorology.
2. To check the efficiency of heat engine.
3. To obtain the work value of the fuel used.

They are of great use in predicting defects in the performance of the engine.

ENTROPY OF A PERFECT GAS

Consider 1 gm mole of a perfect gas at a pressure P volume V and temperature T. When dQ amount of heat is supplied to it, it expands

$\therefore$ Change of entropy (ds) $= \dfrac{dQ}{T}$

$\Rightarrow dQ = Tds \qquad \rightarrow \text{ I}$

From Ist law of thermodynamics $dQ = dU + Pdv \qquad \rightarrow \text{ II}$

from I & II we get $Tds = du + Pdv$

but $\quad dU = C_V dT$

$\therefore Tds = C_V dT + PdV$

$\Rightarrow ds = \dfrac{C_V dT + PdV}{T}$

$\Rightarrow ds = \dfrac{C_V dT}{T} + \dfrac{PdV}{T} \rightarrow III$

Expression of entropy in terms of volume and temperature :- In this P is to be eleminated we know that,

PV = RT

$\Rightarrow \quad P = \dfrac{RT}{V} \qquad \therefore$ IIIrd step becomes,

$\Rightarrow ds = \dfrac{C_v dT}{T} + \dfrac{RT}{V}\dfrac{dv}{T}$

$$\Rightarrow \quad ds = \frac{C_v dT}{T} + R\frac{dv}{V} \qquad \rightarrow IV$$

The initial and final values of pressure, volume and temperature are represented by P_i, V_i, T_i & P_f, T_f, V_f respectively. S_i and S_f represent initial and final entropies of the gas. The change of entropy $(S_f - S_i)$ when the gas changes from intial state to final state can be obtained by integrating the above equation with proper limits.

$$S_f - S_i = \int_{S_i}^{S_f} ds = C_v \int_{T_i}^{T_f} \frac{dT}{T} + R \int_{V_i}^{V_f} \frac{dV}{V}$$

$$= C_v \, \log_e \left(\frac{T_f}{T_i}\right) + R \, \log_e \left(\frac{V_f}{V_i}\right)$$

$$= 2.303 \left[C_v \, \log_{10} \left(\frac{T_f}{T_i}\right) + R \, \log_{10} \left(\frac{V_f}{V_i}\right) \right] \qquad \rightarrow V$$

Expression of entropy interms of temperature and pressure :- In this volume is to be eliminated we know that, $PV = RT$

$$\Rightarrow \quad Pdv + Vdp = RdT$$

$$\Rightarrow \quad dv = \frac{RdT - VdP}{P}$$

By substituting the above value in the IIIrd equation we get,

$$ds = \frac{C_v dT}{T} + \frac{P}{T} \left(\frac{RdT - VdP}{P}\right)$$

$$\Rightarrow \quad ds = \frac{C_v dT}{T} + \frac{RdT}{T} - \frac{VdP}{T}$$

$$\Rightarrow \quad ds = (C_v + R)\frac{dT}{T} - \frac{VdP}{T}$$

But $C_p - C_v = R$

$$\Rightarrow \quad C_p = R + C_v \quad \text{and from} \quad PV = RT$$

$$\Rightarrow \quad \frac{V}{T} = \frac{R}{P}$$

$$\therefore \quad ds = C_p \frac{dT}{T} - R\frac{dp}{P} \qquad \text{by integrating above step with proper limits}$$

we get, $$S_p - S_i = C_p \int_{T_i}^{T_f} \frac{dT}{T} - R \int_{P_i}^{P_f} \frac{dP}{P}$$

$$= C_p \, \log_e \left(\frac{T_f}{T_i}\right) - R\log_e \left(\frac{P_f}{P_i}\right)$$

$$= 2.303 \left[C_p \, \log_{10} \left(\frac{T_f}{T_i}\right) - R\log_{10} \left(\frac{P_f}{P_i}\right) \right]$$

Expression of entropy in terms of pressure and volume :- In this from $PV = RT$ we get,

$$\Rightarrow \quad Pdv + Vdp = RdT$$

$$\Rightarrow \quad dv = \frac{Rdt - VdP}{P}$$

$$\therefore ds = C_v \frac{Pdv - VdP}{RT} + \frac{pdv}{T}$$

But $PV = RT$ and $\quad \dfrac{P}{T} = \dfrac{R}{V}$

$$\therefore ds = C_v \left(\frac{Pdv + vdP}{Pv} \right) + \frac{Rdv}{V}$$

$$= C_v \left(\frac{dv}{v} + \frac{dp}{p} \right) + \frac{Rdv}{v}$$

$$= (C_v + R) \frac{dv}{v} + C_v \frac{dp}{p}$$

$$ds = C_p \frac{dv}{v} + C_v \frac{dp}{p}$$

by integrating the above step with proper limits we get,

$$S_f - S_i = C_p \int_{V_i}^{V_f} \frac{dv}{V} + C_v \int_{P_i}^{P_f} \frac{dP}{P}$$

$$= C_p \log_e \left(\frac{V_f}{V_i} \right) + C_v \log_e \left(\frac{P_f}{P_i} \right)$$

$$= 2.303 \left[C_p \log_{10} \left(\frac{V_f}{V_i} \right) + C_v \log_{10} \left(\frac{P_f}{P_i} \right) \right]$$

The above expressions can be used for finding the change of entropy of a perfect gas.

UNIT-3

THERMODYNAMIC POTENTIALS AND MAXWELL'S EQUATIONS

Thermodynamic Potentials

For the complete description of the thermodynamic system some relations are required. For this purpose we can use some functions known as thermodynamic potentials. Thermodynamic Potentials are energy functions formed by combining the basic thermodynamically variables pressure, volume, temperature & entropy. We know that a conservative mechanical system is in equilibrium when the potential energy of the system is minimum. Similarly, a thermodynamical system will be in equilibrium when the thermodynamic potentials are having minimum values.

These are

1) Internal Energy (U)

2) Helmholtz function (F)

3) Enthalpy or total heat function (H)

4) Gibbs function (G)

Internal Energy (U):

The internal energy is sum of K.E and P.E of the molecules. K.E arises due to motion of the molecules and potential energy due to intermolecular force of attraction. When a system passes from one state to another, the change in internal energy does not depend upon the path followed but depends only on initial and final states. The physical significance of internal energy is the capacity to do work plus the capacity to release heat.

From the I law of thermodynamics $\qquad dQ = dU + dW$

$$dU = dQ - dW$$

From the II law of thermodynamics $\qquad dQ = TdS \qquad\qquad (\because dS = dQ/T)$

$$dW = PdV$$

$$\therefore dU = TdS - PdV \qquad\qquad (1)$$

Taking partial differentiation of internal energy with respect to variables S and V

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad , \qquad\qquad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

As dU is a perfect differential

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad\qquad (2)$$

This is Maxwell's I thermodynamic relation.

Helmholtz function (F):-

The Helmholtz energy is a measure of the ability of the system to do useful work (non-mechanical work) in an isothermal process.

We now that from I & II law of thermodynamics

$$dU = TdS - PdV$$

In the Isothermal process, the temperature is constant.

$$dU = d(TS) - PdV$$

$$dU - d(TS) = -PdV$$

$$d(U - TS) = -PdV$$

$$dF = -dW$$

U - TS = F is known as Helmholtz function.

From The above equation the external work done on the system is equal to the decrease in Helmholtz function.

Change in Helmholtz function,

$$dF = dU - d(TS)$$
$$= dU - TdS - SdT$$
$$= TdS - PdV - TdS - SdT \qquad \{\because dU = TdS - PdV\}$$
$$dF = -PdV - SdT$$

Taking partial differentiation of F with respect to variables V & T.

$$\left(\frac{\partial F}{\partial T}\right)_V = -S$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -P$$

As dF is prefect differential then

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T$$

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

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \qquad (3)$$

This equation is known as Maxwell's II thermodynamic relation.

Enthalpy (H):

H gives the heat content at constant pressure just as internal energy U gives the heat content a constant volume. So this is called as heat function at constant pressure. The enthalpy is a measure of the ability of the system to do useful work (non-mechanical) in an isothermal process.

Enthalpy is mathematically expressed as

$$H = U + dV$$

Change in enthalpy $dH = dU + d(PV)$
$$= dU + PdV + VdP$$
$$= TdS - PdV + PdV + VdP$$
$$dH = TdS + VdP$$

Partial differentiation of dH with respect to the variables S & P

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

As dH is a perfect differential,

$$\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad\qquad (4)$$

This equation is known as Maxwell's III thermodynamic relation.

Gibb's function (G):

G is the energy liberated or absorbed in reversible process at constant pressure and constant temperature.

From the definition of enthalpy

$$H = U + dV$$

Change in enthalpy

$$dH = dU + d(PV)$$
$$dH = dU + PdV + VdP$$
$$= TdS - PdV + PdV + VdP$$
$$dH = TdS + VdP$$

If the process is isothermal

$$TdS = d(TS)$$
$$dH = d(TS) + VdP$$
$$dH - d(TS) = VdP$$
$$d(H - TS) = VdP$$

Here H-TS = G is known as Gibb's function.

G remains constant if a thermodynamic process remains isothermal as well as isobaric.

dG = 0 when the process is isobaric (dP = 0)

$$G = H - TS$$
$$dG = dH - d(TS)$$
$$= dH - TdS - SdT$$
$$dG = TdS + VdP - TdS - SdT$$
$$dG = VdP - SdT$$

Partial differentiation with respect to variables P & T

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \ , \ \left(\frac{\partial G}{\partial P}\right)_T = V$$

As dG is a perfect differential

$$\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T$$

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

This equation is known as Maxwell's IV thermodynamic relation.

Importance:

1) The change in internal energy when a system passes from one state to another is independent of path

followed between two states ($dU = U_f - U_i$)

2) The decrease in Helmholtz function gives the work done on the system in an isothermal process.

$dF = - PdV = -W$.

3) The change in enthalpy is equal to the quantity of heat given to the system for the change of state of constant pressure.

$dH = TdS + VdP$

$dH = TdS$ $\{\because dP = 0\}$

$dH = dQ$

4) If the process is isothermal and isobaric then $dG = 0$ i.e., G = constant.

> *Note: - TVPS, SVPT, TPVS, -SPVT*

IMPORTANCE OF THERMODYNAMICAL FUNCTIONS

Thermodynamic functions are of practical importance in studying the equilibrium conditions a system.

(i) 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.

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

$dF = 0$ as $dF = - P\,dV - S\,dT$

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

(iii) 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.

(iv) 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.

CLAUSIUS - CLAYPERON EQUATION: -

The Clausius - Clayperon latent heat equation relates the change in melting point (or) Boiling point with change in pressure, the equation can be derived from Maxwell's 2nd thermodynamic relation which is expressed as

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

Multiplying both sides by 'T'

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

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

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

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial V}\right)_T \qquad (\because T\partial S = \partial Q)$$

Here ∂Q represents the heat absorbed at constant temperature that is ∂Q is latent heat.

Let unit mass of a substance under constant temperature is converted from one state to another state absorbing on amount of heat L (Latent heat). Suppose the specific volume in the I and II states be V_1 & V_2 then $\partial V = V_2 - V_1$.

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

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

This is Clausius - Clayperon Latent heat equation. This relation gives the change in melting point or Boiling pint with change in pressure.

Applications of Clausius - Clayperon Equation:

1. This equation can be used to study the variation of the boiling point of liquid with pressure. When a liquid boils that is change from liquid state to gases state there is an increase in volume

   ie,$V_2 - V_1 = $ +ve

   $$\frac{\partial P}{\partial T} \text{ is also a + ve Quantity}$$

   This means that the boiling point of a liquid rises with the increase of pressure. Hence under reduced pressure, the liquid boils at lower temperature.

2. Melting point of a solid is classified into two classes with respect to pressure.

   a) When $V_2 > V_1$ (as for wax and sulphur)

   $$\frac{\partial P}{\partial T} \text{ is a + ve Quantity}$$

   This means that the melting point of such substances increases with increase of pressure.

   b) When $V_2 < V_1$ (as for ice, gallium and bismuth)

   $$\frac{\partial P}{\partial T} \text{ is a - ve Quantity}$$

   This means that the melting point of such substances decreases with increase of pressure.

3. This equation also explains the relegation of ice (when the two pieces of ice are pressed they form a single piece). This is called relegation.

THE RATIO BETWEEN TWO SPECIFIC HEATS C_P AND C_V:-

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 1^0c when the volume of the 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 one gram gas through 1^0c when the pressure of the gas is kept constant.

     We show that $\dfrac{C_p}{C_v} = \gamma$ using Maxwell's relations

The coefficient of volume elasticity $\quad E = \dfrac{\text{Stress}}{\text{Volume Strain}} = \dfrac{dP}{\left(\dfrac{-dV}{V}\right)} \quad \Rightarrow E = -V\left(\dfrac{dP}{dV}\right)$

     The adiabatic elasticity E_s (S = constant), $\quad E_S = -V\left(\dfrac{\partial P}{\partial V}\right)_S$

     And isothermal elasticity E_T (T = constant), $\quad E_T = -V\left(\dfrac{\partial P}{\partial V}\right)_T$

From the 1st and 2nd TdS equations,

$$TdS = C_V dT + T\left(\dfrac{\partial P}{\partial T}\right)_V dV$$

$$TdS = C_P dT - T\left(\dfrac{\partial V}{\partial T}\right)_P dP$$

If entropy constant, dS = 0 then $\quad 0 = C_V dT + T\left(\dfrac{\partial P}{\partial T}\right)_V dV$

$$C_V dT = -T\left(\dfrac{\partial P}{\partial T}\right)_V dV$$

$$C_V dT = -T\left(\dfrac{\partial P}{\partial T}\right)_V dV$$

$$C_P dT = T\left(\dfrac{\partial V}{\partial T}\right)_P dP$$

$$C_P dT = T\left(\dfrac{\partial V}{\partial T}\right)_P dP$$

$$\dfrac{C_P}{C_V} = \dfrac{-\left[\left(\dfrac{\partial V}{\partial T}\right)_P\right]}{\left(\dfrac{\partial P}{\partial T}\right)_V}\left(\dfrac{\partial P}{\partial V}\right)_S$$

     From 2nd and 4th Maxwell's thermodynamic relations

$$\dfrac{C_P}{C_V} = \left[\dfrac{\left(\dfrac{\partial S}{\partial P}\right)}{\left(\dfrac{\partial S}{\partial V}\right)_T}\right]\left(\dfrac{\partial P}{\partial V}\right)_S$$

$$\frac{C_P}{C_V} = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_S$$

$$= \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{\left(\frac{-E_S}{V}\right)}{\left(\frac{-E_T}{V}\right)} \qquad \left\{ \because \left(\frac{\partial P}{\partial V}\right)_S = \frac{-E_S}{V} \right\}$$

$$\frac{C_P}{C_V} = \frac{E_S}{E_T} = \gamma$$

∴The ratio between two specific heats is equal to the ratio between the elasticities.

DIFFERENCE BETWEEN TWO SPECIFIC HEATS C_P & C_V:

Specific heat at constant pressure, $C_P = \left(\frac{\partial Q}{\partial T}\right)_P$

Specific heat at constant volume, $C_V = \left(\frac{\partial Q}{\partial T}\right)_V$

From 2nd law of thermodynamics dQ = TdS

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad \text{and} \qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\frac{C_P - C_V}{T} = \left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V\right] \rightarrow (1)$$

Let S = S(V, T),

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

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

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

From equation (1) and from Maxwell's 2nd thermodynamic relation.

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

But $PV = RT$

$$\frac{\partial P}{\partial T} = \frac{R}{V} \quad ; \quad \frac{\partial V}{\partial T} = \frac{R}{P}$$

$$\frac{C_P - C_V}{T} = \frac{R}{V} \cdot \frac{R}{P}$$

$$C_P - C_V = T\frac{R^2}{PV} = T\frac{R^2}{RT} = R$$

Finally C_p - C_v = R

JOULE-KELVIN (JOULE-THOMSON'S) EFFECT:

When a gas under a constant high pressure is passed through a porous plug to a region of constant low pressure, there is a change in its temperature this is called as Joule- Kelvin effect (or) Joule

Thomson's effect. The following points are observed.

porous plug

i)   All the gases when passed through a porous plug suffer a change in temperature. At ordinary temperatures all gases except hydrogen and helium suffer a fall in temperature (cooling effect).while hydrogen and Helium suffer a slight rise in temperature (Heating effect).

ii) The change in temperature is directly proportional to the pressure difference on the two sides of the plug.

iii) As the initial temperature of a gas rises the cooling effect diminishes. At a certain initial temperature known as inversion temperature, the cooling effect is changed into heating effect.
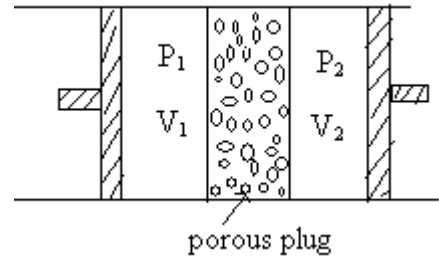
Expression for Joule-Kelvin co-efficient: -

When a gas suffers Joule-Kelvin effect the total enthalpy of the gas remains constant.

i.e.., $H = U + PV = $ constant

$dH = dU + PdV + VdP = 0$

$dU + PdV + VdP = 0$

$TdS - PdV + PdV + VdP = 0$

$TdS + VdP = 0$ ----- (1)

Let $S = S(P,T)$

$$dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \rightarrow (2)$$

Substitute (2) in (1)

$$T\left[\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT\right] + VdP = 0$$

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

$$T\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial Q}{\partial T}\right)_P dT + VdP = 0$$

$$T\left(\frac{\partial S}{\partial P}\right)_T dP + C_P dT + VdP = 0 \qquad \left\{\because \left(\frac{\partial Q}{\partial T}\right)_P = C_P\right\}$$

$$C_P dT = -T\left(\frac{\partial S}{\partial P}\right)_T dP - VdP$$

From Maxwell's fourth relation,

$$C_P dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P dP - VdP\right]$$

$$C_P dT = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] dP$$

$$\frac{dT}{dP} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$$

This is the expression for cooling produced by Joule-Kelvin effect.

$\left(\frac{\partial T}{\partial P}\right)_H = +Ve$, there is a cooling effect

$\left(\frac{\partial T}{\partial P}\right)_H = 0$, There is neither cooling nor heating

$\left(\frac{\partial T}{\partial P}\right)_H = -Ve$, There is a heating effect

Joule -Kelvin coefficient for a perfect (ideal) gas:

$$PV=RT$$

Differentiate with respect to T, at constant pressure,

$$V = \frac{RT}{P}$$

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

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\frac{R}{P} - V\right]$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{RT}{P} - V\right]$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{PV}{P} - V\right]$$

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

Hence Joule-Kelvin effect for a perfect gas is zero.

JOULE - KELVIN EFFECT FOR A VANDERWALL'S GAS (REAL GAS): -

Vander Wall's equation for gas is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

Differentiate with respect to T at constant pressure

$$\left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P + (V - b)\left[\frac{-2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right] = R$$

$$\left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_P - (V - b)\left[\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P\right] = R$$

$$\left(\frac{\partial V}{\partial T}\right)_P\left[\left(p + \frac{a}{V^2}\right) - (V - b)\frac{2a}{V^3}\right] = R$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\left[\left(p + \frac{a}{V^2}\right) - (V - b)\frac{2a}{V^3}\right]}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R(V-b)}{\left[\left(p+\frac{a}{V^2}\right)(V-b) - \frac{2a}{V^3}(V-b)^2\right]}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R(V-b)}{\left[RT - \frac{2a}{V^3}(V-b)^2\right]} \qquad a,b \ll V$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R(V-b)}{\left[RT - \frac{2a}{V^3}.V^2\right]} = \frac{R(V-b)}{\left[RT - \frac{2a}{V}\right]} = \frac{R(V-b)}{RT\left[1 - \frac{2a}{RTV}\right]} = \frac{(V-b)}{T\left[1 - \frac{2a}{RTV}\right]}$$

$$T\left(\frac{\partial V}{\partial T}\right)_P = (V-b)\left[1 - \frac{2a}{RTV}\right]^{-1}$$

$$= (V-b)\left[1 + \frac{2a}{RTV}\right]$$

Neglecting the higher powers

$$T\left(\frac{\partial V}{\partial T}\right)_P = V + \frac{2a}{RTV} - b - \frac{2a}{RTV}$$

Neglecting $\frac{2a}{RTV}$

$$T\left(\frac{\partial V}{\partial T}\right)_P = V + \frac{2a}{RT} - b$$

$$\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] = \frac{2a}{RT} - b$$

From (3) $C_P\left(\frac{\partial T}{\partial P}\right)_H$

$$C_P\left(\frac{\partial T}{\partial P}\right)_H = \frac{2a}{RT} - b$$

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$$

When $b = \frac{2a}{RT}$, then $\left(\frac{\partial T}{\partial P}\right)_H = 0$

      The temperature at which the Joule-Thomson coefficient becomes zero is called as Inversion temp. (T_i) that is gas on passing through porous plug suffers neither cooling nor heating i.e., the corresponding temp. is T_i.

If $\left(\frac{\partial T}{\partial P}\right)_H = 0$ When $T = T_i\left(b = \frac{2a}{RT}\right)$ Neither cooling nor heating

If $\left(\frac{\partial T}{\partial P}\right)_H = +ve$ When $T < T_i\left(b < \frac{2a}{RT}\right)$ Cooling effect

if $\left(\frac{\partial T}{\partial P}\right)_H = -ve$ When $T > T_i\left(b > \frac{2a}{RT}\right)$ Heating Effect

Relation Between T_i & T_c :

$T_i = \dfrac{2a}{Rb}$ where a & b are Vander Waal's constant

The critical temperature

$$T_C = \frac{8a}{27Rb}$$

$$\therefore \frac{T_i}{T_C} = \frac{\dfrac{2a}{Rb}}{\dfrac{8a}{27Rb}} = \frac{2a}{Rb} \cdot \frac{27Rb}{8a} = \frac{27}{4}$$

i.e., the ratio is independent of the nature of the gas.

$$T_i = \left(\frac{27}{4}\right)T_C = 6.75 T_C$$

<div align="center">

UNIT-4

LOW TEMPERATURE PHYSICS

</div>

PHASE CHANGE OF FIRST ORDER

The term 'change of state' gives the details of the change in the thermodynamic state in terms of pressure (P), volume (V) and temperature (T). In thermodynamics, change of phase means transitions of matter. The term 'phase' is the equilibrium condition of a homogeneous substance. For example, Ice, Water and Steam are the three phases of a single substance. So the phases are the various states in which a material can exist. A first order phase change is one in which the emission or absorption of heat taking place without any change in temperature.

For example, when a given mass of water is heated at constant pressure, the internal energy of water increases as the temperature increases. At boiling point (100°C or 373 K), the internal energy is absorbed and changes the phase of water into gaseous phase (temperature remaining constant).

The amount of energy supplied to convert water into steam at the boiling point is called specific latent heat of vaporization L_v (2.26 x 10^6 J/kg).

Similarly, when a given mass of water is cooled, its internal energy decreases uniformly till freezing point (0°C or 273 K). Now after giving out 3.34 x 10^5 J/kg of internal energy, the water is converted into solid phase called ice.

The amount of energy released to convert water into ice at the freezing point is called specific latent heat of fusion L_f.

In this way water exists in the solid phase upto 0°C, in liquid from 0°C to 100°C and the gaseous phase above 100°C at atmospheric pressure. For each substance there is a set of temperature and pressure at which any of the two states of the three (solid, liquid and gas) may exist in equilibrium.

We consider the following curves

(i) Liquid-Vapour curve

For this curve, we consider an enclosure filled with liquid and its saturated vapour. The vapour pressure of saturated vapour depends upon temperature alone. This increases with the increasing temperature. In figure (1), this is shown by OA known as curve of vaporization. The substance above is liquid while below OA is in vapour state.

(ii) Fusion curve

The solid may coexist in equilibrium with the liquid. The pressure-temperature curve in this case is known as fusion curve. This is denoted by OB. To the left side of the curve, the substance exist in solid state and liquid state towards right side.
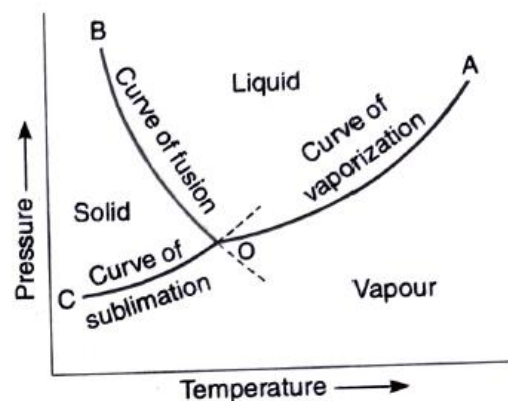
(iii) Sublimation curve

The solid may coexist with vapour in equilibrium. The temperature and pressure at which the solid and vapour may exist in equilibrium is shown by curve OC. The curve is known as sublimation curve. Above OC, the substance is wholly in solid state and below it in vapour state.

Thus, the pressure on the substance determines the range of temperature for which the substance exists in a given phase. When all the three curves are plotted on the same graph with the same scale, they intersect at point O. The point O is called the triple point. Hence, triple point may be defined as *a point at which the temperature and pressure are such that the solid, liquid and vapour phase coexist in equilibrium*. The corresponding temperature and pressure are called triple point temperature (T_t) and triple point pressure (P_t)

METHODS TO PRODUCE LOW TEMPERATURES

1. Freezing mixture: -

The mixture of salt +ice is called freezing mixture. Some ice melts by absorbing heat from salt and the salt starts dissolving in the water. The total heat is drawn from the mixture itself. Therefore, its temperature decreases. The lowest temperature attained by this method is called Eutectic temperature. This is independent of pressure. With sodium chloride (NaCl) freezing mixture, the Eutectic temperature gives - 22^0C. Potassium Hydroxide (KOH) freezing mixture gives - 65^0C.

2. Evaporation under reduced pressure: -

When a thermally insulated liquid is allowed to evaporate (or) boil under reduced pressure, the necessary heat is taken from the liquid itself. So its temperature decreases. The amount of cooling depends upon the nature of the liquid and rate of evaporation. This method depends upon the pressure. Liquid Hydrogen gives - 255.78^0C and liquid Helium gives - 268.9^0C.

3. Adiabatic Expansion of Compressed gas: -

When the compressed gas is suddenly made to expand adiabatically against external pressure, the energy required for this external work is taken from the internal energy of the system. So, the temperature decreases. Kapitza used this method to liquify H_2 and Helium.

4. Joule Thomson expansion: -

When a gas is made to pass through a porous plug or narrow orifice from high pressure region to low pressure region, the temperature decreases. This is known as Joule Thomson expansion. Any gas below inversion temperature exhibits cooling effect.

5. Adiabatic demagnetization: -

When a magnetized paramagnetic substance is demagnetized under adiabatic condition its temperature falls. This method is used to produce a temperature of order of 10^{-4} K (or) below it.

JOULE THOMSON EFFECT- POROUS PLUG EXPERIMENT

When a gas under a higher constant pressure region is passed through a porous plug (like cotton, wool) to a lower constant pressure region, the gas suffers a change in temperature. This effect is known as Joule kelvin (or) Joule Thomson effect.

Porous plug experiment: - The experiment consists of a thermally insulated cylinder PQ containing porous plug. It is provided with two non-conducting pistons A and B. The porous plug separates the cylinder into two parts. P_1, V_1, T_1 are pressure, volume and temperature of the gas in left part, P_2, V_2, T_2 are
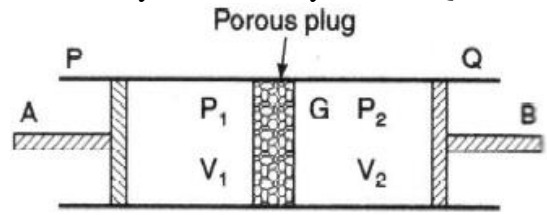
corresponding values on the right part respectively, such that $P_1>P_2$. The gas is compressed by moving the piston A towards the porous plug, then certain mass of the gas passes through the porous plug to the lower pressure side. The molecules of the gas are drawn apart and hence the gas suffers a change in temperature.

Work done by the piston A on the gas in the left compartment $= P_1V_1$

Work done on the piston B by the gas in the right compartment $= P_2V_2$

Net work done by the gas $= P_2V_2 - P_1V_1$

Let, initial internal energy $= U_1$

Final internal energy $= U_2$

Decrease in internal energy $= U_1 - U_2$

As the system is thermally isolated, this work must have been done at the expense of the internal energy of the gas hence we can write,

$$P_2V_2 - P_1V_1 = U_1 - U_2$$
$$P_2V_2 - P_1V_1 = U_1 - U_2$$
$$P_2V_2 + U_2 = P_1V_1 + U_1$$
$$P_1V_1 + U_1 = P_2V_2 + U_2$$

i.e., H = U + PV = Constant   (1)

Hence enthalpy H is constant in Joule-Kelvin effect.

In addition to this some internal work is done against the intermolecular force of attraction. If we assume the gas to obey the Vander waal's equation, the attraction between the molecules is equal to internal pressure $\dfrac{a}{V^2}$, where a is constant and V is volume.

The work done against the inter molecular force of attraction

$$W_2 = \int_{V_1}^{V_2} \frac{a}{V^2} dv = a\int_{V_1}^{V_2} \frac{1}{V^2} dv = a\left(\frac{-1}{V}\right)_{V_1}^{V_2}$$

$$W_2 = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) \dots\dots\dots\dots \quad . \quad (2)$$

Total work done by the gas is

$$= p_2 V_2 - p_1 V_1 + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)\dots\dots \qquad (3)$$

From Vander waal's equation we have ,

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

$$\Rightarrow PV - Pb + \frac{a}{V^2}.V - \frac{ab}{V^2} = RT$$

$$\Rightarrow PV - Pb + \frac{a}{V} = RT$$

$$\Rightarrow PV = RT + Pb - \frac{a}{V} \qquad --------(4)$$

For the values in the left compartment we have write,

$$P_1 V_1 = RT + P_1 b - \frac{a}{V_1} \qquad --------(5)$$

For the values in the right compartment we have write,

$$P_2 V_2 = RT + P_2 b - \frac{a}{V_2} \qquad --------(6)$$

$$P_2 V_2 - P_1 V_1 = RT + P_2 b - a/V_2 - RT - P_1 b + a/V_1$$

$$P_2 V_2 - P_1 V_1 = RT + P_2 b - \frac{a}{V_2} - RT - P_1 b + \frac{a}{V_1}$$

$$P_2 V_2 - P_1 V_1 = (P_2 - P_1)b + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) \qquad \therefore \dots\dots (7)$$

Substituting equation (7) in equation (3)

$$W = (P_2 - P_1)b + \left(\frac{a}{V_1} - \frac{a}{V_2}\right) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$W = (P_2 - P_1)b + 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) \qquad (8)$$

Since values $\frac{1}{V_1}$ and $\frac{1}{V_2}$ are small we can use the approximate relation

$$pV = RT \Rightarrow \frac{1}{V} = \frac{p}{RT}$$

for the values of left and right compartments we can write ,

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

Substituting these values in equation (8) we get

$$W = (p_2 - p_1)b + \frac{2a}{RT}(p_1 - p_2)$$

$$W = (p_1 - p_2)\left(\frac{2a}{RT} - b\right) \qquad \text{............} \quad \textbf{(9)}$$

As the system isothermally insulated this work is drawn from the internal energy of the gas. If is the specific heat at constant pressure and dT is the change in temperature, the heat energy drawn by the gas is

$$C_p dT \ \text{calories} = C_p dTJ \ \text{joules} \ \text{-------------} \ (10)$$

From equations (9) and (10) we can write,

$$C_p dTJ = (P_1 - P_2)\left[\frac{2a}{RT} - b\right]$$

$$dT = \frac{(P_1 - P_2)}{C_p J}\left[\frac{2a}{RT} - b\right] \qquad \text{----------}(11)$$

It is the required expression for Joule-Kelvin effect

(i) If $\frac{2a}{RT} = b$, then dT=0, now the gas suffers neither heating effect nor cooling effect. The corresponding temperature is called inversion temperature .It is denoted by T_i

$$\frac{2a}{RT_i} = b \Rightarrow T_i = \frac{2a}{Rb} \qquad \text{......} (12)$$

 (ii) If $T > T_i$, then dT is negative, now the gas suffers heating effect.

(iii) If $T < T_i$, then dT is positive now the gas suffers cooling effect.

Results of Joule Kelvin effect:-

1. All gases suffer a change in temperature after passing through porous plug.

2. At ordinary temperature all gases (except H_2 and He) exhibit cooling effect while H_2 and He exhibit heating effect.

3. The change in temperature is directly proportional to difference in pressure on both sides of the porous plug.

4. At a particular temperature known as inversion temperature. Joule Kelvin effect changes its sign i.e, cooling effect is converted into heating effect.

Perfect gas:

    We know that for Joule-Kelvin effect, $P_1V_1 + U_1 = P_2V_2 + U_2$

Perfect gas obeys Boyle's law $P_1V_1 = P_2V_2$ Hence $U_1 = U_2$

If K_1 and ρ_1 be the Kinetic and potential energies on L.H.S and K_2 and ρ_2 be the similar quantities on R.H.S

$$K_1 + \rho_1 = K_2 + \rho_2$$

But there is no force of attraction between the molecules of a perfect gas.

$$\therefore \rho_1 = \rho_2 \Rightarrow K_1 = K_2 \quad and \quad T_1 = T_2 = \rho_2$$

Therefore Joule kelvin effect is zero for perfect gas.

Real gases: For real gases $P_1V_1 \neq P_2V_2$

i) Below the Boyle temperature: The product PV decreases as the pressure P increases i.e. $P_2V_2 > P_1V_1$ OR $U_1 > U_2$

Thus on passing through porous plug, the internal energy of the gas will decrease. Hence the temperature falls (cooling effect)

ii) At Boyle's temperature: The gas strictly obey Boyle's law. Thus $P_2V_2 = P_1V_1$ OR $U_2 = U_1$

i.e. the temperature of the gas remains constant.

iii) Above Boyle's temperature: The product PV increases as the pressure increases. Thus $P_1V_1 > P_2V_2$ OR $U_2 > U_1$

The temperature of the gas will rise (heating effect)

JOULE EXPANSION/FREE EXPANSION:

It is a free expansion in which the gas expands into volume and hence thus no external work in this expansion. Internal work is done by the gas against the intermolecular attraction. The contribution of net external work may be a cooling effect (or) a heating effect depending upon the initial temperature of the gas. Generally this effect is not observed due to the large heat of the apparatus.

JOULE KELVIN EXPANSION:

In this expansion the gas under high pressure is forced to pass through porous plug to a region of lower pressure. Hence external work is done on the gas, as well as by the gas in addition to internal work there may be a cooling effect (or) heating effect depending upon the initial temperature of the gas. At ordinary temperature gases (except hydrogen and helium) show cooling effect.

ADIABATIC EXPANSION:

In this expansion the compressed gas is suddenly released to atmosphere, the gas performs external work against the pressure of the atmosphere. The process is so fast that no appreciable heat flows into thegas from the surroundings. Hence the external work is drawn from the internal energy of the gas. Thus the gas cools. So in adiabatic expansion the cooling is due to external work.

S.no	Joule expn	Adiabatic expn	Joule - Kelvin expn
1.	It is free expn. The gas expands into Vacuum	Compressed gas is suddenly released to atomsphere and expands	The gas passes through porous plug from high pressure region to low pressure region
2.	No external work is done	The gas performs external work against atmospheric pressure. In this expn no heat transfer takes place	In this external work is done on the gas and by the gas in addition to internal work
3.	The internal work is done by the gas against inter molecular attraction. There may be heating effect or cooling effect depending upon the initial temp of the gas	The external work is drawn from the internal energy of the gas. Therefore the gas cools.	There may be heating effect or cooling effect depending upon the initial temp of the gas cooling effect takes place when the temp of the gas $< T_i$ heating effect takes place when the temp of the gas $> T_i$ There is neither heating nor cooling effect if temp of the gas $= T_i$
4.	It is irreversible	It is reversible	It is irreversible
5.	A perfect gas shows no change in temp but real gas always shows cooling effect	Both real and ideal gases always show cooling effect	A perfect gas shows no change in temp. but real gas shows both cooling & heating effects

LIQUEFACTION OF AIR - LINDE'S PROCESS

Linde's air liquefier makes use of the principle of regenerative cooling. The Linde air liquefier is shown in figure. It consists of two compressors P_1 and P_2. The first Compressor compresses the incoming air from 1 to 20 atmospheres. The compressed air is passed through cold water bath to remove the heat of compression and then allowed to pass through caustic potash, calcium chloride and phosphorus penta-oxide to remove carbon di-oxide and water. This is done because carbon di-oxide and water vapours will solidify before the air is liquefied and choke the whole system.

Air free from carbon di-oxide and water vapour now enters the second compressor where it is compressed to 200 atmospheric pressure. The compressed air then passes through the spiral tube kept in freezing mixture. The temperature of air here falls to - 20°C.

The air thus, cooled at high pressure enters the liquefying section and suffers Joule-Thomson expansion at nozzle N_1. As the gas at this stage is allowed to expand to 20 atmospheric pressure, its temperature falls to about -70°C. The nozzle N_2 is closed at this stage. So the cooled air flows through the wider tube B back to the compressor P_2 where it is again compressed to 200 atmospheric pressure. In its way to compressor P_2, it cools the incoming gas in tube A. The principle of regenerative cooling takes place and after few cycles, the air is cooled to sufficiently low temperature (-183°C). Now the second nozzle N_2 is opened. The air expands to one atmospheric pressure and is liquefied. The liquid air is collected in Dewar flask D.

Fig. (4)
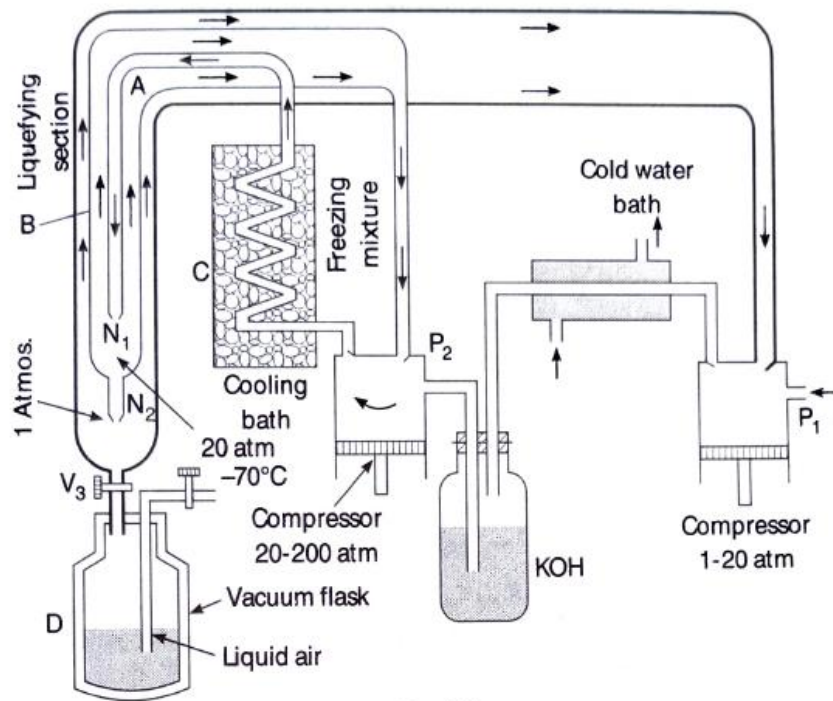
ADIABATIC DEMAGNETIZATION:-

In order to obtain very low temperatures, the adiabatic demagnetization process is used. A paramagnetic substance contains molecules which are lying in an orderly manner when the substance is magnetized. The molecules are set in the direction of magnetic field. Due to this the temperature of the substance rises. This magnetized substance is kept at very low temperature. Now if the magnetic field is removed, the temperature of the substance decreases.

The paramagnetic substance 'P' i.e., gadolinium sulphate is suspended in vessel A. The vessel A is filled with liquid helium evaporated at low pressure. The temperature of helium vapour becomes at about 1K. The vessel A is placed in another vessel B which is filled with liquid He at 1K. The vessel B is placed in vessel C which is filled with liquid H2 at 20 K. A strong magnetic field is applied to magnetize the paramagnetic substance. Coils M are placed to measure the temperatures by susceptibility measurements. Due to magnetization, the temperature of paramagnetic

substances slightly increases. But this heat is absorbed by He gas, from it, the heat is transferred to liquid He. Again the temperature of paramagnetic substance becomes 1K. Using vacuum pump helium gas is removed from vessel A. Due to this the paramagnetic substance is thermally isolated. Now the applied
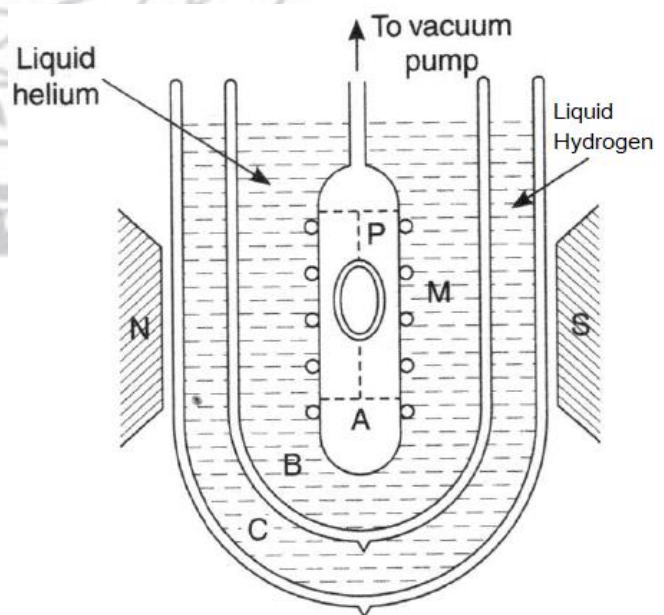
magnetic field is switched off. Due to this adiabatic demagnetization the temperature of the paramagnetic substance decreases.

Expression:-

When a paramagnetic substance is magnetized its molecules try to align in the direction of the field and work is done. If the paramagnetic substance is placed in the magnetic field of magnetic flux density 'B'.

Now the intensity of magnetization per gram mole 'I' of the substance changes by 'dI'. The work done by the field on the substance is 'BdI'. When the substance is demagnetized the work done by the substance is ' -BdI'.

From I law of thermodynamics $dQ = dU + dW$

$$dQ = dU - BdI \qquad ---- (1) \qquad [\because dW = -BdI]$$

From Maxwell's III thermodynamic relation

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

To obtain similar relation substitute -B for P and I for V.

i.e., P = -B, V = I

$$-\left(\frac{\partial T}{\partial B}\right)_S = \left(\frac{\partial I}{\partial S}\right)_B$$

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\frac{\partial I}{\partial T}}{\frac{\partial S}{\partial T}}\right)_B$$

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{\left(\frac{\partial I}{\partial T}\right)_B}{\left(\frac{\partial S}{\partial T}\right)_B} \qquad \to (2)$$

'm' be the mass of the specimen and C_B is its specific heat of constant field.

Then

$$\frac{\partial S}{\partial T} = \frac{1}{T}\left(\frac{\partial Q}{\partial T}\right) = \frac{mC_B}{T} \qquad \to (3)$$

Substitute equation (3) in equation (2)

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{\left(\frac{\partial I}{\partial T}\right)_B}{\frac{mC_B}{T}}$$

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{mC_B}\left(\frac{\partial I}{\partial T}\right)_B \qquad \to (4)$$

$$\text{but susceptibility } \chi = \frac{\text{Intensity of magnetization of specimen}}{\text{Intensity of magnetizing field}}$$

$$\chi = \frac{I}{B} \qquad \to (5)$$

According curies law the paramagnetic susceptibility of a substance is inversely proportional to the absolute temperature.

$$\chi \propto \frac{1}{T} \Longrightarrow \chi = \frac{C}{T} \qquad \to (6)$$

Here, C = curies constant

From equation (5) and (6)

$$\frac{I}{B} = \frac{C}{T}$$

$$I = \frac{CB}{T} \qquad \to (7)$$

Substitute equation (7) in equation (4)

$$\frac{\partial T}{\partial B} = -\frac{T}{mC_B}\left(\frac{\partial}{\partial T}\left(\frac{CB}{T}\right)\right)$$

$$= -\frac{TCB}{mC_B}\left(\frac{\partial}{\partial T}\left(\frac{1}{T}\right)\right)$$

$$= -\frac{TCB}{mC_B}\left(\frac{-1}{T^2}\right)$$

$$= \frac{CB}{mC_B T}$$

$$\partial T = \frac{C}{mC_B T}.B\,\partial B$$

If T_i and T_f be the initial and final temperatures of the substance, when magnetic field is increased form B_i to B_f.

$$\int_{T_i}^{T_f}\partial T = \frac{C}{mC_B T}\int_{B_i}^{B_f} B\,\partial B$$

$$[T]_{T_i}^{T_f} = \frac{C}{mC_B T}\left[\frac{B^2}{2}\right]_{B_i}^{B_f}$$

$$T_f - T_i = \frac{C}{mC_B T}\left[\frac{B_f{}^2}{2} - \frac{B_i{}^2}{2}\right]$$

If the magnetic field is switched off i.e., $B_f = 0$

$$T_f - T_i = \frac{C}{mC_B T}\left[-\frac{B_i{}^2}{2}\right]$$

$$T_f - T_i = \frac{-B_i{}^2 C}{2mC_B T}$$

$$T_f - T_i = \frac{-B_i{}^2 K}{2TC_B} \rightarrow (8) \quad \text{where } \frac{C}{m} = K, \text{Curies constant per unit mass}$$

The negative sign in equation (8) represents the fall in temperature in adiabatic demagnetization.

APPLICATIONS OF SUBSTANCES AT LOW TEMPERATURES

The behavior of matter at low temperature is different from that at ordinary temperatures. This fact is used in the fields of science, research and industry. Some of the applications are as follows.

1. The conductors at low temperature become super conductors. There are used in electrical appliances to reduce power losses.

2. Liquid O_2 is used in hospitals for respiration.

3. Liquid O_2 with charcoal is used for the manufacture of explosives.

4. Below 90K most of the chemical reactions will be stopped. So, the substances can be preserved without purification below 90K.

5. Ammonia, Sulphur dioxide (SO_2) and Freon in liquid state are used in refrigerators and air conditioners.

6. The calorimeters used for measuring specific heats at low temperature make use of liquid air, liquid oxygen and liquid hydrogen.

7. The paramagnetic character of oxygen O_2 increases with the decrease of temperature. This is used to measure temperatures near absolute zero.

UNIT-V

QUANTUM THEORY OF RADIATION

Thermal radiation

The process of heat transfer in which no material medium required is termed as radiation. We receive heat from the sun even though no material medium (in empty space) between the sun and earth. So the process of heat transfer from a body by virtue of its temperature without the involvement of the medium is called radiation. The heat by radiation is transported by electromagnetic waves because these waves can travel through vacuum. The radiation emitted by a body by virtue of its temperature is called *thermal radiation*. Thermal radiation is a particular range of electromagnetic radiation.

Thermal radiation wavelength band extends from 0.1×10^{-6} m to 100×10^{-6} m. It includes -Ultraviolet wavelength band from 0.1×10^{-6} m to 0.38×10^{-6} m, Visible wavelength band from 0.38×10^{-6} m to 0.76×10^{-6} m and Infra-red region from 0.76×10^{-6} m to 100×10^{-6} m.

- Thermal radiation is an inherent property of all bodies.
- According to Prevost's theory of heat exchanger, everybody emits and absorbs radiant energy continuously as long as its temperature is above 0 K.
- The thermal radiation emitted by a body, per unit time and per unit surface area, depends on the nature of surface and on its temperature.
- The emission rate is small at low temperature and it increases rapidly as fourth power of absolute temperature with temperature.
- At ordinary and moderate high temperatures, mostly the longer waves (infra-red) are emitted but at very high temperatures shorter waves are also emitted.

Properties of thermal radiation

Thermal radiation has the following properties as light.

(i) It travels through empty space with light velocity.

(ii) It travels in straight lines as light,

(iii) It obeys reflection, refraction and total internal reflection laws.

(iv) It exhibits the phenomenon of interference, diffraction and polarization.

(v) It exerts a small finite pressure on the surface when it incident on it. This is called as pressure of thermal radiation.

(vi) It obeys the inverse square law.

Terminology in Radiation:

(1) Spectral energy density： Spectral energy density for a particular wavelength is the energy per unit volume per unit range of wavelength. .

(2) Total energy density: Total energy density of thermal radiation at any point is the total radiant energy per unit volume around that point due to all wavelengths.

(3) Emissive power: The emissive power of a body, at a given temperature and for a given wavelength, is defined as the radiant energy emitted per second by unit surface area of the body per unit wavelength range. This is denoted by e_λ..

(4) Absorptive power: The absorptive power of a body, at a given temperature and for a given wavelength, is defined as the ratio of the radiant energy absorbed per second by unit surface area of the body to the total energy falling per second on the same area. This is denoted by a_λ

   Let Q be the amount of thermal radiations falling on a body in a given time. Suppose Q_1, Q_2 and Q_3 be the amounts of radiations reflected, absorbed and transmitted by the body respectively in the same time t.

Reflectance (r_λ)

This is defined as the ratio of amount of thermal radiations reflected by the body in a given time to the total amount of radiations failing on the body in that time. i.e.,

$$r_\lambda = \frac{Q_1}{Q}$$

Absorptance (a_λ)

This is defined as the ratio of amount of radiations absorbed by the body in given time to the total radiations falling on the body in that time. i.e.,

$$a_\lambda = \frac{Q_2}{Q}$$

Transmittance (t_λ)

This is defined as the ratio of amount of radiations transmitted by the body in a given time to the total radiations falling on the body in that time. i.e.,

$$t_\lambda = \frac{Q_3}{Q}$$

A body may have different reflectance, absorptance and transmittance for radiations of different wavelengths. But for a particular wavelength

$$r_\lambda + a_\lambda + t_\lambda = \frac{(Q_1+Q_2+Q_3)}{Q} = 1$$

BLACK BODY AND ITS RADIATION:

   A perfectly black body is one which completely absorbs all the radiations of all wavelengths incident on it. According to Kirchhoff's l aw, a body which is capable of absorbing radiation must also be capable of emitting all possible wavelengths. So a perfectly black body is a good absorber as well as a good radiator. Since it neither reflects nor transmits any radiation, it appears black. At a suitable high temperature, it emits all kinds of wavelengths. This is called full radiation or total radiation.

As the radiation emitted by black body is rich in maximum possible wavelengths and hence, such radiations are known as *full radiation* or *total radiation.* The wavelength of emitted radiation by a black body depends only on its temperature and is independent of the material of the body.

The nearest approach of a black body is lamp black or platinum black as there is no perfect blackbody available in nature. According to Kirchhoff a conducting enclosure maintained at constant temperature can be taken as a black body.
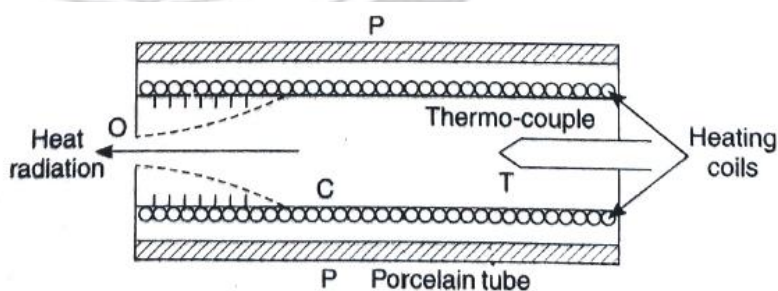
FERRY'S BLACK BODY

It is in the form of double walled conducting sphere. The interspace between the walls is evacuated to prevent loss of heat by conduction and convection. It has a small hole O and a conical projection P just outside the hole O. It is lamp-blacked inside and nickel polished outside. When the radiation is incident on the hole, it passes inside the enclosure. The radiation suffers multiple reflections inside the enclosure and is completely absorbed. There is hardly any possibility of the radiation to get out except by direct reflection from the surface opposite to the hole. This is eliminated by the projection P. In this way any radiation that enters the body does not escape and is absorbed. Therefore, the body appears as perfectly black. Here the hole behaves very closely like a black body. If the enclosure is heated to a definite temperature, it is filled with black radiation having all possible wavelengths.
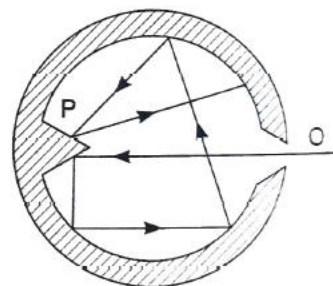
WIEN'S BLACK BODY

It consists of a long metallic tube C blackened inside and surrounded by concentric porcelain tubes P, P. The tube is heated by electric current passing in the coil (Heating coil) wound around it. The temperature of the central part of the tube is measured by thermocouple T. Heat radiations emerge out of the hole O. The radiation from the inner chamber can be limited with the help of diaphragms shown by dotted lines. The hole acts as a black body radiator.

ENERGY DISTRIBUTION IN BLACK BODY RADIATION

According to Stefan's law the total amount of radiant energy by a black body per unit area per second due to all wavelengths is directly proportional to the fourth power of absolute temperature. But it does not give any information on energy distribution. The distribution of energy in black body radiation for different wavelengths and at various temperatures was determined experimentally by

Lummer and Pringsheim in 1899. They used an electrically heated chamber with a narrow aperture as the black body. The temperature of the heated enclosure was measured by thermocouple. In this the radiation from a black body O was focused on a slit S by a concave mirror M_1. The slit S is placed at the focus of another concave mirror M_2. So that radiation after reflection from M_2 becomes parallel. The parallel beam of radiation is allowed to incident on a fluorspar prism ABC. The prism produces the spectrum of radiations.
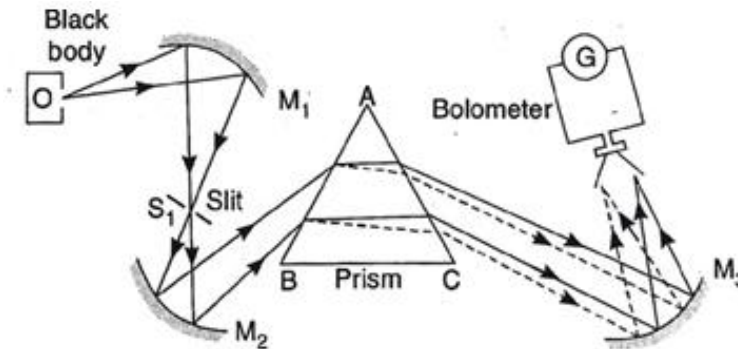
The emergent dispersed beam is incident on concave mirror M_3. This mirror focuses different wavelengths at different angles. The radiations are denoted by means of Bolometer which consists of a Galvanometer. The deflection produced in the Galvanometer gives the intensity of radiation.

Instead of rotating Bolo-Meter to obtain different wavelengths maxima the mirror M_3 was rotated about a vertical axis and different maxima were detected for the same wavelength at different temperatures.

The experiment was repeated for the same wavelengths at different temperatures. Then a graph was drawn between energy E_λ and wavelength λ at different temperatures. The curves so obtained as shown in figure.

λ in microns (10^{-6} m)
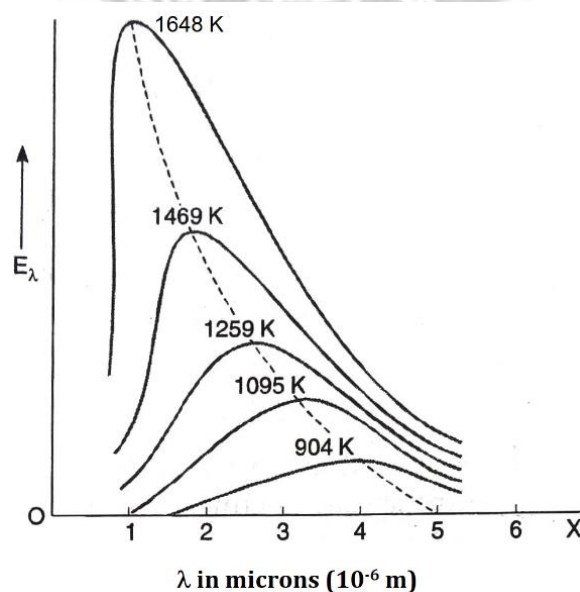
Experimental results

(1) The emission from a black body at any temperature is composed of radiation from all wavelengths.

(2) At a given temperature, the energy is not uniformly distributed. As the temperature of the black body increases, the intensity of radiation for each wavelength increases. This shows that the total amount of energy radiated per unit area per unit time increases with rise of temperature.

(3) The total energy of radiation at any temperature is the area between the curve and the horizontal axis.

The increase in area is found in accordance with the Stefan's law.

$$E = \int_0^\infty E_\lambda \, d_\lambda = \sigma T^4$$

(4) The amount of radiant energy emitted is small at very short and very long wavelengths.

(5) The wavelength corresponding to the maximum energy represented by the peak of the curve shifts towards shorter wavelengths as the temperature increases. This is called Wien's displacement law. According to this law,

$\lambda_m \, T$ = constant

This shows that as the temperature is increased, the black body emits the radiation of shorter wavelengths such that the product of temperature T and maximum wavelength is a constant.

LAWS OF THERMAL RADIATION

Kirchhoff's Law

This law states that at a given temperature, the ratio of emissive power to the absorptive 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.

Energy absorbed by the body = energy emitted by the body

$$a_\lambda \, dQ_\lambda = e_\lambda \, d_\lambda$$
$$\frac{a_\lambda}{e_\lambda} = \frac{d_\lambda}{dQ_\lambda}$$

$\frac{d_\lambda}{dQ_\lambda}$ depends only on temperature and for a given temperature it is constant

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.,

$$E \propto T^4$$
$$E = \sigma T^4$$

where σ is called as Stefan's constant. It has a value 5.67 x 10⁻⁸ W m⁻² K⁻⁴

This law obeys only when the medium surrounding the black body.

Wien's Law

Wien showed that the maximum energy point shifts towards the shorter wavelengths side when the temperature of the body is raised.

$$\lambda_m T = \text{constant}$$

where is the wavelength corresponding to maximum energy emission from a black body at absolute temperature T. Wien's formula agrees for short wavelengths region only.

He also stated that the maximum energy emitted by a black body is proportional to the fifth power of its absolute temperature.

$$(E_\lambda)_{max} \propto T^5$$

$$or \; \frac{(E_\lambda)_{max}}{T^5} = \text{Constant}$$

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_λ as

$$E_\lambda = C_1 \lambda^{-5} e^{\frac{C_2}{\lambda T}}$$

Rayleigh-Jean's Law

According to Rayleigh-Jean's law, the energy distribution in the thermal spectrum is given by

$$E_\lambda = \frac{8\pi k T}{\lambda^4}$$

where k is Boltzmann constant.
Rayleigh-Jeans formula agrees for long wavelength region only.

Planck's Law

On the basis of quantum theory, Planck derived the following formula for the energy distribution in thermal spectrum

$$E_\lambda = \frac{8\pi h c}{\lambda^5 (e^{\frac{hc}{\lambda k T}} - 1)}$$

where h is Planck's constant, c, the velocity of light and k being the Boltzmann constant.

It should be remembered that unlike Wien's formula and Rayleigh-Jeans formula, Planck's formula is applicable for entire range of wavelengths.

WIEN'S DISPLACEMENT LAW:

Statement: The wavelength corresponding to maximum emission of energy is inversely proportional to the absolute temperature T.

$$\text{i.e. } \lambda_m \, \alpha \, \frac{1}{T}$$

$$\lambda_m T = \text{constant}$$

$$= 0.2896 \times 10^{-2} \text{ mK}$$

Proof:

Consider a spherical enclosure with perfectly reflecting walls and capable of expansion radially out wards. It is filled with diffused radiation of energy density 'u' at temperature T ^0K. If 'V' is the volume of the enclosure $U = uV$

Suppose the radiation expands inside the spherical enclosure due to the moving of the walls radially outwards with a velocity of v. If 'dV' is the change in volume then work done $dW = PdV$ which is drawn from internal energy.

We know that from I law of thermodynamics $dQ = dU + dW$.

Since the process is adiabatic, $dQ = 0$

$$0 = d(uV) + dW$$
$$0 = d(uV) + PdV$$
$$\Rightarrow udV + Vdu + PdV = 0$$

From electromagnetic theory, $P = \dfrac{u}{3}$

$$\Rightarrow udV + Vdu + \frac{u}{3}dV = 0$$

$$u\,dV\left[1+\frac{1}{3}\right] + Vdu = 0$$

$$u\,dV\frac{4}{3} + Vdu = 0$$

Dividing by uV

$$\frac{u\,dV}{uV}\frac{4}{3} + \frac{Vdu}{uV} = 0$$

$$\frac{dV}{V}\frac{4}{3} + \frac{du}{u} = 0$$

On intergrating we get

$$\frac{4}{3}\log V + \log u = \text{constant}$$

$$\log V^{4/3} + \log u = \text{constant}$$

$$\log u\,V^{4/3} = \text{constant}$$

$$u\,V^{4/3} = \text{constant} \text{-------------(1)}$$

According to Stephan's law

$$u \propto T^4$$

$$u = \sigma T^4 \text{--------- (2)}$$

substitute (2) in (1)

$$\sigma T^4\,V^{4/3} = \text{constant}$$

$$T^4\,V^{4/3} = \text{constant}$$

$T\ V^{1/3} = $ constant   ------- (3)

We have to find the change in wavelength of a ray due to reflection from expanding walls due to Doppler effect.

'AO' is the incident ray, incident at an angle of incidence θ. Suppose the crest of the wave strikes at the wall at A. This crest will be reflected along 'AC'. Let AC = λ. But as the reflected crest reaches C the next crest will reach A in time T. During this time the wall has to move to the position M through a distance υT. So the path of reflected crest will be along ABD. This path (AB+BD = λ_1) is greater than the path of the first reflected wave (AC = λ).
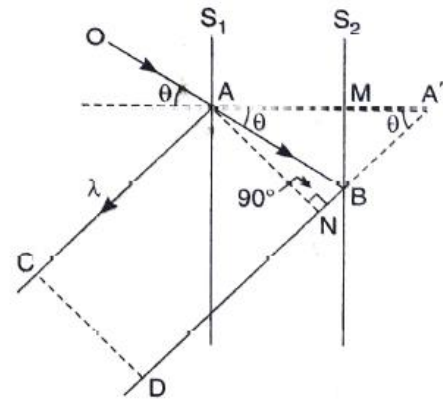
The change in wavelength due to one reflection = $\lambda_1 - \lambda$

$$= AB+BD-AC$$
$$= AB+BN+ND-AC$$
$$= AB+BN$$
$$= A'B+BN = A'N$$
$$= AA'\cos\theta$$
$$= 2\,\upsilon T\cos\theta$$

Change in wavelength due to one reflection = $2\,\upsilon\,\dfrac{\lambda}{C}\,\cos\theta$

Every ray inside the spherical enclosure undergoes repeated reflections. Consider the path of a single ray between two successive reflections, say at *A* and *B*, the wave travels a distance *2r* cos θ.

Time interval between two successive reflections = $\dfrac{2\,r\,\cos\theta}{C}$

Number of reflections per second = $\dfrac{C}{2\,r\,\cos\theta}$

Number of reflections made in 'dt' time = $\dfrac{C}{2\,r\,\cos\theta}\,dt$

So number of reflections made in 'dt' time = $\dfrac{C}{2\,r\,\cos\theta}\,\dfrac{dr}{\upsilon}$ --------- (5) $\left[\because v=\dfrac{dr}{dt}\right]$

Change in wavelength in one reflection X number of reflections in dt time

$$=2\,\upsilon\,\frac{\lambda}{C}\,\cos\theta\ \times\frac{C}{2\,r\,\cos\theta}\,\frac{dr}{\upsilon}$$
$$d\lambda = \lambda\,\frac{dr}{r}$$
$$\frac{d\lambda}{\lambda} = \frac{dr}{r} \qquad\qquad \rightarrow (6)$$

Volume of the sphere $V = \dfrac{4}{3}\pi r^3$

By differentiating, we get,

$$dV = \frac{4}{3}\pi.3r^2 dr = 4\pi r^2 dr$$

$$\frac{dV}{V} = \frac{4\pi r^2 dr}{\frac{4}{3}\pi r^3}$$

$$\frac{dV}{V} = 3\frac{dr}{r}$$

$$\frac{dr}{r} = \frac{1}{3}.\frac{dV}{V} \qquad \rightarrow (7)$$

Substituting equation (7) in equation (6)

$$\frac{d\lambda}{\lambda} = \frac{1}{3}.\frac{dV}{V}$$

Integrating on both sides

$$log = logV + logK$$

$$log\lambda = logKV^{1/3}$$

$$\lambda = V^{1/3}K$$

$$V^{1/3} = \frac{\lambda}{K} \qquad\qquad --- (8)$$

Substitute (8) & (3) $T\ \frac{\lambda}{K} =$ constant

$$\lambda T = \text{constant}$$

This is Wien's displacement law.

PLANCK'S RADIATION LAW:

Planck's hypothesis: - In 1900 Max Planck introduced the concept of quantum theory of radiation. He made the assumptions.

1. A Black body radiator contains simple harmonic oscillations of all possible frequencies.

2. The oscillators cannot emit or absorb energy continuously.

3. Emission or absorption of energy takes place in discrete amount i.e., the energy of an atomic oscillator of frequency υ can have only certain values $0, h\upsilon, 2h\upsilon, 3h\upsilon\ldots$

   This is an integral multiple a small unit of energy $h\upsilon$ called the Quanta or photon.

   In General for an oscillator of frequency υ the possible values of the energy are given by

   $E = nh\upsilon$

Where n is positive integer, h = Planck's constant.

Average energy of an oscillator:

Let N be the total number of Planck's oscillators and E be their total energy then the average energy per Planck's oscillator $\bar{E}$ is given by

$$\bar{E} = \frac{E}{N} \qquad\qquad \rightarrow (1)$$

Let there be N_0, N_1, N_2 ... N_r, ... etc., oscillators having energy $0, E, 2E, 3E, \ldots rE \ldots$ respectively. Now we have

$$N = N_0 + N_1 + N_2 + N_3 + \ldots\ldots + N_r + \ldots\ldots \qquad \rightarrow (2)$$

$$E = 0 + N_1 + 2E\,N_2 + 3N_3 + \ldots\ldots + r\,N_r + \ldots\ldots \qquad \rightarrow (3)$$

According to Maxwell's distribution formula the number of oscillators having energy $\bar{E}$ is given by

$$N_r = N_0\ e^{-rE/KT} \qquad\qquad \rightarrow (4)$$

   Where K is Boltzmann constant.

Substitute N_1, N_2, N_3 ... from equation (4) in equation (2)

$$N = N_0 + N_0 e^{-E/KT} + N_0 e^{-2E/KT} + N_0 e^{-3E/KT} + \ldots$$

$$N = N_0\ [1 + e^{-E/KT} + e^{-2E/KT} + e^{-3E/KT} + \ldots]$$

$$N = \frac{N_0}{1 - e^{-E/KT}} \qquad\qquad \rightarrow (5) \qquad \left[\because 1 + x + x^2 \ldots = \frac{1}{1-x} = (1-x)^{-1} \right]$$

Substitute the values N_1, N_2, N_3, ... in equation(3)

$$E = EN_0 e^{-E/KT} + 2EN_0 e^{-2E/KT} + 3EN_0 e^{-3E/KT} + \ldots$$

$$= EN_0 e^{-E/KT} \left[1 + 2e^{-E/KT} + 3e^{-2E/KT} + \ldots \right]$$

$$= \frac{EN_0 e^{-E/KT}}{\left[1 - e^{-E/KT} \right]^2} \qquad\qquad \rightarrow (6) \qquad \left[\because 1 + 2x + 3x \ldots = \frac{1}{(1-x)^2} \right]$$

Substitute equation (5) & equation (6) in equation (1) we get average energy of an oscillator.

$$\bar{E} = \frac{\dfrac{EN_0 e^{-E/KT}}{\left(1 - e^{-E/KT}\right)^2}}{\dfrac{N_0}{\left(1 - e^{-E/KT}\right)}}$$

$$= \frac{E e^{-E/KT}}{1 - e^{-E/KT}}$$

$$= \frac{E}{\left[\dfrac{1 - e^{-E/KT}}{e^{-E/KT}} \right]} = \frac{E}{e^{E/KT} - 1}$$

$$= \frac{h\upsilon}{\left[e^{h\upsilon/KT} - 1 \right]} \qquad\qquad \rightarrow (7)$$

Planck's Formula:

   The number of oscillations per unit volume in frequency range υ and $\upsilon + d\upsilon$ is given by

$$f = \frac{8\pi \upsilon^2}{C^3} d\upsilon \qquad\qquad \rightarrow (8)$$

Multiply equation (8) by average energy of oscillator (7) we get the total energy per unit volume belonging to the range $d\upsilon$ is given by

$$E_\upsilon d\upsilon = \frac{8\pi \upsilon^2}{C^3} d\upsilon \frac{h\upsilon}{\left[e^{h\upsilon/KT} - 1 \right]}$$

$$E_\upsilon d\upsilon = \frac{8\pi\upsilon^3 h d\upsilon}{C^3\left[e^{h\upsilon/KT}-1\right]} \qquad\qquad \rightarrow(9)$$

This is known as Planck's radiation law. This law can be expressed in terms of wave length as

$$\upsilon = \frac{C}{\lambda} \;\Rightarrow\; d\upsilon = \frac{-C}{\lambda^2}d\lambda$$

$$|d\upsilon| = \frac{C}{\lambda^2}d\lambda$$

Substitute in equation (9)

$$E_\lambda d\lambda = \frac{8\pi h\left(\dfrac{C}{\lambda}\right)^3\left(\dfrac{C}{\lambda^2}d\lambda\right)}{C^3\left[e^{hc/k\lambda T}-1\right]}$$

$$= \frac{8\pi h\dfrac{C^3}{\lambda^3}\left(\dfrac{C}{\lambda^2}d\lambda\right)}{C^3\left[e^{hc/k\lambda T}-1\right]}$$

$$E_\lambda d\lambda = \frac{8\pi hC\, d\lambda}{\lambda^5\left[e^{hc/k\lambda T}-1\right]}$$

This is called Plank's formula and it agrees with the experimental curves throughout the whole range of wavelengths.

Different laws from Planck's radiation formula

Wien's formula:

For short wavelengths i.e., when λ is very small $\qquad e^{\frac{hc}{K\lambda T}} \gg 1$

So 1 can be neglected when compared to $e^{\frac{hc}{K\lambda T}}$

$$E_\lambda d\lambda = \frac{8\pi hc\, d\lambda}{\lambda^5\left[e^{hc/k\lambda T}\right]}$$

$$E_\lambda d\lambda = \frac{8\pi hc\, e^{-hc/k\lambda T}d\lambda}{\lambda^5}$$

Let $A = 8\pi hc, \quad \dfrac{hc}{K} = B.$

$$E_\lambda d\lambda = \frac{A\, e^{-B/\lambda T}d\lambda}{\lambda^5}$$

This is Wien's formula which agrees with experiment at short wavelengths.

Rayleigh Jeans Formula:

For longer wavelengths i.e., when λ is very large $\frac{hc}{\lambda KT}$ is small and $e^{\frac{hc}{K\lambda T}}$ can be expanded as

$$e^{\frac{hc}{K\lambda T}} = 1 + \frac{hc}{K\lambda T} + \frac{h^2 c^2}{2K^2\lambda^2 T^2} + \ldots\ldots$$

$$= 1 + \frac{hc}{K\lambda T} \qquad [\because \text{neglecting the higher powers}]$$

Substitute in equation (10)

$$E_\lambda d\lambda = \frac{8\pi hcd\lambda}{\lambda^5\left[1+\dfrac{hc}{K\lambda T}-1\right]}$$

$$= \frac{8\pi hcd\lambda}{\lambda^5\left[\dfrac{hc}{K\lambda T}\right]}$$

$$= \frac{8\pi d\lambda}{\left[\dfrac{\lambda^4}{kT}\right]}$$

$$E_\lambda d\lambda = \frac{8\pi kTd\lambda}{\lambda^4}$$

This is Rayleigh Jeans's formula which agrees with experimental values at longer wavelengths

Wien's displacement law from planks law:

According to Planck's radiation formula

$$E_\lambda d\lambda = \frac{8\pi hcd\lambda}{\lambda^5\left[e^{hc/k\lambda T}-1\right]}$$

$$E_\lambda = \frac{8\pi hc}{\lambda^5}\left[e^{hc/k\lambda T}-1\right]^{-1}$$

$$E_\lambda = A.\lambda^{-5}\left[e^{hc/k\lambda T}-1\right]^{-1} \rightarrow (1)$$

$$here\, A = 8\pi hc$$

To find out the wavelength at which the spectrum irradiancy is maximum. We differentiate equation (1) with respect to λ and equate it to zero.i.e.,

$$\frac{\partial E_\lambda}{\partial \lambda} = 0$$

$$\Rightarrow \frac{\partial E}{\partial \lambda} = A\lambda^{-5}\left[(-1)\left[e^{hc/k\lambda T}-1\right]^{-2}e^{hc/k\lambda T}\left[\frac{-hc}{\lambda^2 KT}\right]+A\left[e^{hc/k\lambda T}-1\right]^{-1}\left(-5\lambda^{-6}\right)\right]=0$$

$$\Rightarrow \lambda^{-5}\frac{hc}{\lambda^2 KT}.e^{hc/k\lambda T}\left[e^{hc/k\lambda T}-1\right]^{-2}=5\lambda^{-6}\left[e^{hc/k\lambda T}-1\right]^{-1}$$

$$\Rightarrow \frac{hc}{\lambda^2 KT}.e^{hc/k\lambda T}\left[e^{hc/k\lambda T}-1\right]^{-1}=5\lambda^{-1}$$

$$\Rightarrow \frac{hc}{\lambda^2 KT}.e^{hc/k\lambda T}\left[e^{hc/k\lambda T}-1\right]^{-1}=5\lambda^{-1}$$

$$\Rightarrow \frac{hc}{\lambda KT}.e^{hc/k\lambda T}\left[e^{hc/k\lambda T}-1\right]^{-1}=5$$

Let $\dfrac{hc}{\lambda KT}=x,$ then $x\, e^x\left[e^x-1\right]^{-1}=5$

$$\frac{xe^x}{e^x-1}=5 \Rightarrow \frac{x}{1-\dfrac{1}{e^x}}=5 \Rightarrow \frac{x}{1-e^{-x}}=5$$

$$\Rightarrow \frac{x}{5} = 1 - e^{-x}$$

This equation has two roots x = 0 and x = 4.965

x = 0 is ignored and from x = 4.965 $x = \dfrac{hc}{\lambda KT}$

$$4.965 = \frac{hc}{\lambda KT}$$

$$\lambda T = \frac{hc}{K(4.965)} = \text{Constant}$$

$$\lambda T = \text{Constant}$$

This is Wien's displacement law.

PYROMETERS

Pyrometers are instruments used for measurement of high temperatures. The pyrometers based on the principles of radiation are termed as radiation pyrometers. There are two types of radiation pyrometers:

1. Total radiation Pyrometers
2. Optical Pyrometers (or) Spectral Pyrometers

Total radiation Pyrometers

The instruments which measure total radiation emitted by the body under test are called as total radiation pyrometers. These instruments use Stefan's law to measure temperature.

Optical Pyrometers (or) Spectral Pyrometers

The optical pyrometers compare the intensity of radiation of the body with that of a standard body for a certain wavelength at a known temperature. Optical pyrometers use Wien's displacement law or Planck's law for determining temperature.

Advantages:

(i) They can be used to measure any high temperatures even when the hot body is in accessible.

(ii) They need not be put in contact with the hot body nor raised to the temperature of the body.

(iii) There is no difficulty in extrapolation because radiation laws are valid at all temperatures.

Disadvantages

(i) Their range roughly begins at 6000°C and so temperatures below this limit cannot be measured.

(ii) The temperature obtained by these pyrometers is always less than the actual temperature of the source because they use radiation laws which are true only for black bodies. So the measurements are accurate for black bodies only.

SOLAR CONSTANT

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 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.

It is defined as the rate at which solar energy is received by a black surface per unit area placed normal to the sun radiation at the mean distance of the earth from the sun in the absence of earth's atmosphere. Its value 1340 watt/m^2 (or) 1.92 cal/cm^2/min.

ANGSTROM'S PYRHELIOMETER (Determination of Solar Constant)

Determination of solar constant

The instruments used for the determination of solar constant are called pyrheliometers. Angstrom's pyrheliometer is shown in fig. It consists of two thin exactly similar blackened strips
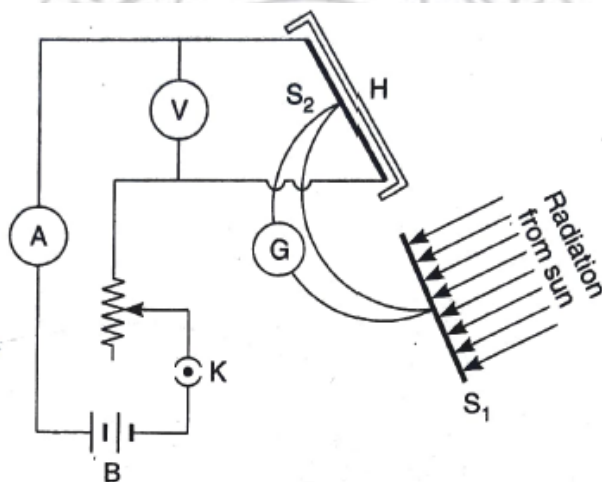
of platinum or constantan S_1 and S_2. The two strips are arranged such that one is open to receive radiation from the sun normally while the other is protected by a double walled shield H. The backs of S_1 and S_2 are connected two junctions of a thermocouple consisting of copper and constantan wire through galvanometer G. The strip S_2 is heated electrically with the help of electric circuit.

Working

When both S_1 and S_2 are at the same temperature then galvanometer G shows no deflection. When S_1 is exposed to radiation from the sun its temperature rises and galvanometer shows deflection. Now current is passed through strip S_2 and its strength is so adjusted that the galvanometer shows no deflection. Under this condition, the temperatures of A and B are the same, i.e., the rate at which heat is supplied to both is same.

The heat energy supplied to strip S_2 can be calculated from the known values of the current and potential difference in the electric circuit. If A be the area of cross-section of the strip and a, its absorption coefficient, then energy absorbed or solar radiation received per minute per square centimeter is known as Solar constant. Hence, solar constant S is given by

$$S = \frac{V \times I \times 60}{A \times a \times 4.2} \, cal \; cm^{-2} \; min^{-1}$$

where V is voltmeter reading in volts and I is ammeter reading.

The experiment was performed several times on the same day under constant sky conditions with different elevations of the sun. The average value of solar constant was then calculated by performing the experiment throughout the year.

The observed value of solar constant S and the true value of solar constant S_0 are connected by the relation

$$S = S_0 \tau^{\sec z}$$

where τ is the transmission coefficient of the atmosphere and z is the zenith distance of the sun (or angular altitude).

Taking logarithms, we have

$$\log S = \log S_0 + \sec z.\log \tau$$

A graph is drawn between log S (on Y-axis) and sec z (on X-axis).

It gives a straight line. The intercept of the straight line on Y-axis gives the value of log S_0. From this, the value of S_0 can be calculated. The value of S_0 comes out to be 1340 Wm^{-2} (1.937 cal cm^{-2} min^{-1} or 80400 J m^{-2} min^{-1}).
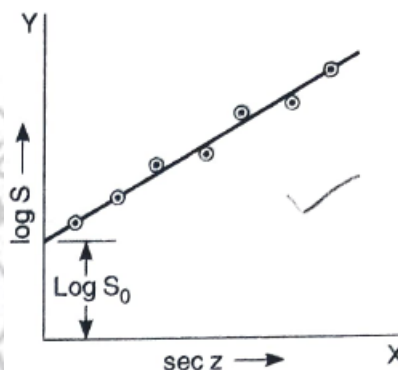
TEMPERATURE OF THE SUN

The sun consists of a central hot core having a temperature of 20 million degrees. The boundary of this central core is a thick shell called the photosphere. Temperature of the sun usually means the temperature of photosphere which is around 6000 K. The next 300 to 400 km thick layer is called as *reversing layer* which contains most of the elements in gaseous state. The extension of reversing layer is *chromosphere.* This is only seen during total solar eclipse. Finally, the outer gaseous layer which extends to more than half a million kilometres is called as *corona.* The different parts are shown in figure. By knowing the value of solar constant and assuming sun as a perfectly black body, the temperature of the sun can be calculated.
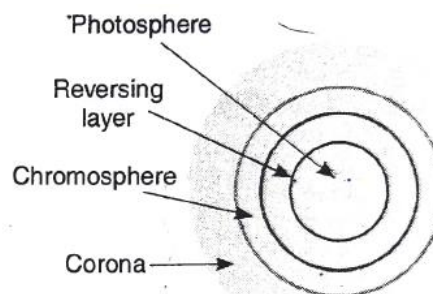
Let R be the radius of the photosphere of the sun. Then its surface area is $4\pi R^2$. If T K be the absolute temperature of the sun, then according to Stefan's law, the amount of energy emitted by the sun per min is given by

$$4\pi R^2 \ \sigma T^4 \times 60$$

where σ is Stefan's constant.

This energy is spread in all directions. Let us consider a sphere of radius r concentric with the sun (r being the distance of the earth from the sun). Then this radiated energy will spread over the surface area $4\pi r^2$. If S is the solar constant, the energy received by the surface $4\pi r^2$ per min is $4\pi r^2 S$. Thus, temperature of sun can be calculated by determining values of S, r, R and σ.

$$4\pi R^2 \ \sigma T^4 \times 60 = 4\pi r^2 S$$

$$T^4 = \frac{4\pi r^2 S}{4\pi R^2 \ \sigma \times 60} = \frac{r^2 S}{R^2 \ \sigma \times 60} = \left(\frac{r}{R}\right)^2 \times \frac{S}{60} \times \frac{1}{\sigma}$$

$$T = \left[\left(\frac{r}{R}\right)^2 \times \frac{S}{60} \times \frac{1}{\sigma}\right]^{1/4}$$

In M.K.S. system $\quad T = \left[\left(\frac{r}{R}\right)^2 \times \frac{S}{\sigma}\right]^{1/4}$