Physics

B. Sc. IV – Semester

Study Material

(As per the syllabus of Adikavi Nannaya University, Rajamahendravaram)

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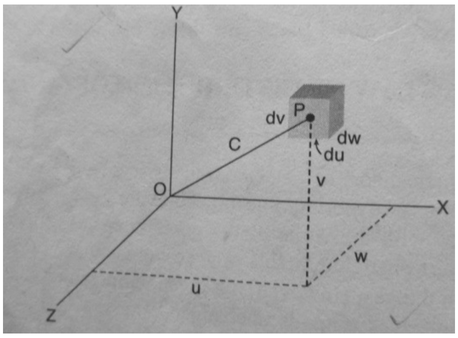
Chapter - I

Kinetic theory of gases

Maxwell's assumptions

1. All the gas molecules in a gaseous system are in random motion.
2. Their velocity ranges from 0 to ∞.
3. In the ideal gas all the molecules are identical.
4. All the gas molecules are in spherical shape and are rigid.
5. There is no force of attraction or repulsion between the molecules.
6. Collisions take place between the molecules and with the walls of the container producing pressure.
7. The collisions are elastic in nature.
8. The molecules travel in straight lines between any two successive collisions.
9. 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.
   & $\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n}$ d= diameter of the molecule n = No. of molecules per unit volume
10. The average density at all points in the gas is same when the gas is in equilibrium condition.
11. Even though the speeds of individual molecules change, a definite no. molecules lie in definite range if the temperature remains constant.
12. The probability of a molecule in a particular range depends on the function of velocity and the range of velocity.
13. The velocities of molecules are resolved in to three mutually perpendicular components. They are independent of each other.

Maxwell's law of distribution of molecular speeds



→ Consider a gaseous system as Cartesian co-ordinate system and its axes are OX, OY and OZ. Take a molecule having a velocity C. This velocity is represented by a vector OP.

→ The velocity C is resolved in to 3 components as u, v & w along X, Y & Z directions respectively as shown in the figure.

So $C^2 = u^2 + v^2 + w^2 \longrightarrow$ (1)

→ If the velocity is in the range C to C+dC, then the velocity components are in the ranges u to u+du, v to v+dv and w to w+dw in the respective directions.

→ The molecules in these ranges lie in the box of volume du.dv.dw.

- The probability of finding a molecule in a range depends on the function of velocity and the range.
- The probability of a molecule in the range u to u+du = f(u).du

The probability of a molecule in the range v to v+dv $= f(v).dv$

The probability of a molecule in the range w to w+dw $= f(w).dw$

- The composite probability is their product $= f(u)\,f(v)\,f(w)du\,dv\,dw \longrightarrow$ (2)
- The composite probability can also be written as function of C i.e. $= \phi(C^2)\,du\,dv\,dw$
- So $\phi(C^2)\,du\,dv\,dw = f(u)\,f(v)\,f(w)du\,dv\,dw$ (or) $\phi(C^2) = f(u)\,f(v)\,f(w) \longrightarrow$ (3)

For a particular value of C $\phi(C^2) = \text{Constant}$

Or $d[\phi(C^2)] = 0$

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

$$f^1(u)\,f(v)\,f(w)\,du + f(u)\,f^1(v)\,f(w)\,dv + f(u)\,f(v)\,f^1(w)\,dw = 0 \longrightarrow (4)$$

Dividing this equation (4) by $f(u)\,f(v)\,f(w)$

$$\frac{f'(u)}{f(u)}\,du + \frac{f'(v)}{f(v)}\,dv + \frac{f'(w)}{f(w)}\,dw = 0 \longrightarrow (5)$$

As C is constant the differential of eqn. (1) is zero

$$2u.du + 2v.dv + 2w.dw = 0$$

Multiplying this eqn. by $\lambda/2$

$$\lambda u.du + \lambda v.dv + \lambda w.dw = 0 \longrightarrow (6)$$

Adding the equations (5) & (6)

$$\left(\frac{f'(u)}{f(u)} + \lambda u\right) du + \left(\frac{f'(v)}{f(v)} + \lambda v\right) dv + \left(\frac{f'(w)}{f(w)} + \lambda w\right) dw = 0 \longrightarrow (7)$$

But u,v & w are independent of each other. So, to satisfy the eqn.(7) each term in the eqn. must be equal to zero

$$\therefore \left(\frac{f'(u)}{f(u)} + \lambda u\right) du = 0 \longrightarrow (8)$$

Similarly $\left(\frac{f'(v)}{f(v)} + \lambda v\right) dv = 0$ & $\left(\frac{f'(w)}{f(w)} + \lambda w\right) dw = 0$

From the eqn.(8) $\frac{f'(u)}{f(u)}\,du = -\lambda u du$

Integrating the above eqn. $\int \frac{f'(u)}{f(u)}\,du = \int -\lambda u du$

$$\log_e f(u) = -\lambda \frac{u^2}{2} + \log_e a$$

Here is $\log_e a$ integration constant. Or $\log_e \frac{f(u)}{a} = -\frac{\lambda u^2}{2}$ or $\frac{f(u)}{a} = e^{\frac{-\lambda u^2}{2}}$

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

Put $\frac{\lambda}{2} = b$ then $f(u) = a\,e^{-bu^2}$

Similarly we can deduce $f(v) = a\,e^{-bv^2}$ & $f(w) = a\,e^{-bw^2}$

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

In order to find the values of constants a & b we will take the probability between the limits $-\infty$ to to $+\infty$ for n no. of molecules .

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

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

Or $\iiint_{-\infty}^{+\infty} a^3\, e^{-\,b(u^2+v^2+w^2)}$ du dv dw = 1 $\longrightarrow$ (9)

But the definite integral value is $\iiint_{-\infty}^{+\infty} e^{-\,b(u^2)}$ du $= \sqrt{\frac{\pi}{b}}$

Similarly $\iiint_{-\infty}^{+\infty} e^{-\,b(v^2)}$ dv $= \sqrt{\frac{\pi}{b}}$ and $\iiint_{-\infty}^{+\infty} e^{-\,b(w^2)}$ dw $= \sqrt{\frac{\pi}{b}}$

∴ eqn. (9) becomes $a^3\sqrt{\frac{\pi}{b}}.\sqrt{\frac{\pi}{b}}.\sqrt{\frac{\pi}{b}} = 1$ (or) $a^3(\frac{\pi}{b})^{\frac{3}{2}} = 1$ (or) $a = \sqrt{\frac{b}{\pi}}$

If $b = \left[\frac{m}{2kT}\right]$ and $a = \sqrt{\left[\frac{m}{2\pi kT}\right]} = \left[\frac{m}{2\pi kT}\right]^{\frac{1}{2}}$

∴ The probability = f(u) f(v) f(w) du dv dw = $a^3\, e^{-\,b(u^2+v^2+w^2)}$ du dv dw

$$\boxed{\text{The probability} = \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}} e^{-\left[\frac{m}{2kT}\right](u^2+v^2+w^2)}\ \text{du dv dw}}$$

This is Maxwell's distribution law.

The probability of molecule in the range from C to C+dC is obtained by taking the volume between the spheres of radii C and C+dC.

This volume = 4π C^2. dC. & du.dv.dw should be replaced by this volume.

$$\text{The probability} = \mathrm{P(C).dC} = \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}} e^{[-\frac{m}{2kT}(C^2)]}\, 4\pi\, \mathrm{C^2.dC.}$$

(or) $$\boxed{\mathrm{P(C).dC} = 4\pi \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}} e^{[-\frac{m}{2kT}(C^2)]}\, \mathrm{C^2.dC.}}$$

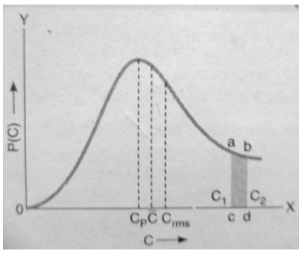
This is the Maxwell's law of distribution of molecular speed in gases.

Here P (C) is the probability function and can be written as

$$\mathrm{P(C)} = 4\pi \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}} e^{[-\frac{m}{2kT}(C^2)]}\, \mathrm{C^2}$$

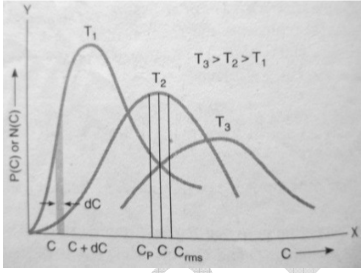
Characteristics of Maxwell's speed distribution curves

At constant temperature:-



1. The speed distribution curve of gaseous system is asymmetric about the peak. Because the highest speed is infinite.
2. As the speed C increases the probability also increases gradually and then decreases.
3. The speed corresponding to the maximum probability is called "most probable speed C_P."
4. The speeds are related as $\boxed{C_{rms} > \bar{C} > C_P}$ Here C_{rms}= rms speed & $\bar{C}$ = Average speed.
5. The area (abcd) below the curve between two speeds C_1 & C_2 gives no. of molecules in that range.
6. The area below the curve gives the total no. of molecules in the system.

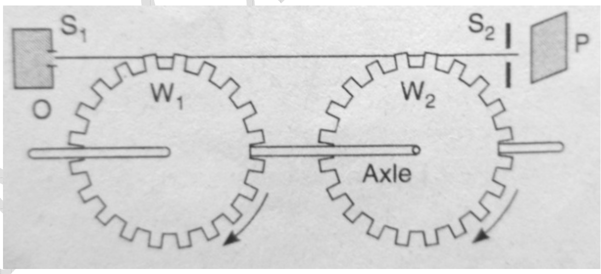
At different temperatures:-



7. Though the system is same if the temperature changes the curve changes.
8. As temperature T increases all the speeds $C_{rms}, \bar{C}$ & C_P increase.
9. As the temperature T increases the peak probability decreases.
10. As the temperature T increases the curves flatten and broaden.
11. The areas below the curves are equal because the no. of molecules are same in the system even though the temperatures are different.

Lammert's toothed wheel experiment (or) Verification of Maxwell's speed distribution law

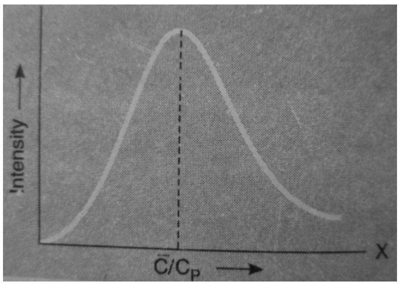
Construction :-



- The experimental arrangement is as shown in the figure.
- It consists of two toothed wheels W_1 and W_2 & each wheel has 50 teeth and 50 slits alternatively.
- The two wheels mounted on the same axle with a separation 'x' such that the slits in the wheel W_2 are lagging 2^0 behind the slits in the wheel W_1.
- Mercury vapour from a oven is passed through a narrow slit $S_1$and is made as a narrow beam.
- These molecules are deposited on the plate P. A micro-photometer is used to measure the intensity of deposit.

Working :-

- First the wheels W_1 and W_2 are set in to rapid rotation and the mercury vapour beam from the slit S_1 is made to fall on wheel W_1 and passed through one of the slits of W_1.
- The molecules of particular speed, after travelling the distance x, will pass through the slit of W_2 that comes in the line of beam after 2^0 of rotation of W_2.
- These molecules are collected on the plate P. The intensity is measured with the micro-photometer.
- The experiment is repeated by rotating the wheels with different speeds.
- As the speed of rotation increases, it takes less time to rotate 2^0. Then a particular higher speed molecules will pass through the slit of W_2 that comes after 2^0 of rotation.



- A graph is drawn by taking intensity on Y-axis and speed of molecules on X-axis. This graph is as shown in the figure. This is similar to the Maxwell's speed distribution curve.

Transport phenomena

1. Different parts of gas may have different velocities. Because of this, relative motion takes place between different gas layers until the gas attains equilibrium position. So, transport of momentum takes place from higher velocity region to lower velocity region. This produces the viscosity in the gas.
2. Different parts of gas may be at different temperatures. In order to attain equilibrium position, relative motion takes place between different gas layers. So, transport of kinetic energy takes place from higher temperature region to lower temperature region. This produces the conduction in the gas.
3. Different parts of gas may have different densities. To attain equilibrium position, the gas molecules travel from high density region to low density region. This gives rise to the phenomenon of diffusion.

These are called transport phenomena.

Viscosity of gases

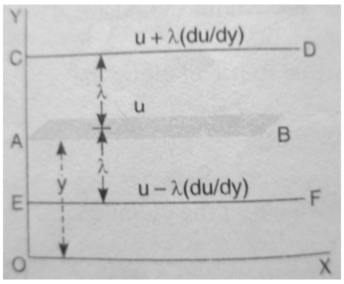
Consider a gas system as different layers parallel to x-axis. The velocity of molecules in the layers increase as moved up. Let 'du' be the change in velocity between two layers separated by a distance 'dy'. Then velocity gradient = $\frac{du}{dy}$

If, A is the area of contact between the layers, then viscosity or viscous force $F = \eta \frac{du}{dy} . A$

Here η = Coefficient of viscosity.

$$\boxed{F = \eta \frac{du}{dy}} \longrightarrow \quad (1)$$ If the area is unity i.e. A = 1

- Consider the gas layer AB having velocity u. Take two more layers CD and EF, above & below AB layer, at a distance λ having velocities $(u + \lambda \frac{du}{dy})$ and $(u - \lambda \frac{du}{dy})$ respectively. Here λ is mean free path.



- Let the no. of molecules per unit volume is 'n', mass of each molecule is 'm' and average speed of molecules be $\bar{C}$.
- The molecules have velocity components in 6 directions.

So, the no. of molecules moving in one direction per unit area & per unit time = $\frac{n\,\bar{C}}{6}$.

Mass moving in one direction = $\frac{m.n\,\bar{C}}{6}$.

Momentum in the down ward direction of molecules in the layer CD that cross AB layer per unit area in unit time $P_1 = \frac{mn\bar{C}}{6} . (u + \lambda \frac{du}{dy})$

Similarly, momentum in the up ward direction of molecules in the layer EF that cross AB layer per unit area in unit time $P_2 = \frac{mn\overline{C}}{6}.(u - \lambda\frac{du}{dy})$

The change of momentum per unit area in unit time

$$F = P_1 - P_2 = \left[\frac{mn\overline{C}}{6}.(u + \lambda\frac{du}{dy})\right] - \left[\frac{mn\overline{C}}{6}.(u - \lambda\frac{du}{dy})\right] = \frac{1}{6}.mn\overline{C}.2\lambda\frac{du}{dy}$$

$$\boxed{F = \frac{1}{3}.mn\overline{C}.\lambda\frac{du}{dy}} \longrightarrow (2)$$

But, the change of momentum produces the viscosity. So,eqns. (1) & (2) are equal. $\therefore\ \eta\frac{du}{dy} = \frac{1}{3}.mn\overline{C}.\lambda\frac{du}{dy}$ (or) $\boxed{\eta = \frac{1}{3}.mn\overline{C}.\lambda = \frac{1}{3}.\rho\overline{C}.\lambda}$

Here mn = ρ = density of gas

But $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$ $\therefore$ $\boxed{\eta = \frac{1}{3}.mn\overline{C}.\frac{1}{\sqrt{2}\pi d^2 n} = \frac{m\overline{C}}{3\sqrt{2}\pi d^2}}$

Thermal conductivity

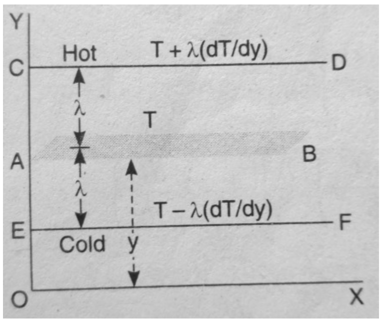
Consider a gas system as different layers parallel to x-axis. The temperature of molecules in the layers increase as moved up. Let ‘dT’ be the change in temperature between two layers separated by a distance ‘dy’. Then temperature gradient = $\frac{dT}{dy}$

If, A is the area through which heat flows, then quantity of heat flow in time t, $Q = K\frac{dT}{dy}.A.t$

Here K = Coefficient of thermal conductivity.

$\boxed{Q = K\frac{dT}{dy}} \longrightarrow$ (1) If the area is unity i.e. A = 1 & time is unity i.e. t =1

- *(**Note** :- In gases heat flows by the method of convection. But here conduction was taken. Because the same no. of molecules, move from upper layers in down ward direction and from lower layers in the up ward direction. So, it can be considered that the heat is flowing with out the movement of the molecules i.e. in the method of conduction.)*



- Consider the gas layer AB having temperature T. Take two more layers CD and EF, above & below AB layer, at a distance λ having temperatures $(T + \lambda\frac{dT}{dy})$ and $(T - \lambda\frac{dT}{dy})$ respectively. Here λ is mean free path.
- Let the no. of molecules per unit volume is ‘n’, mass of each molecule is ‘m’ and average speed of molecules be $\bar{C}$.
- The molecules have velocity components in 6 directions.

So, the no. of molecules moving in <u>one direction per unit area & per unit time</u> = $\frac{n\overline{C}}{6}$.

Mass moving in one direction = $\frac{m.n\overline{C}}{6}$.

But, the quantity of heat in a body Q = mst

Here m = mass, s = specific heat & t = temperature

But for a gas of constant volume Specific heat (s) = Specific heat at constant volume (c_v)

$\therefore \quad Q = mc_vt$

The amount of heat flowing in the down ward direction from the layer CD that cross AB layer per unit area in unit time $Q_1 = \left(\frac{mn\bar{C}}{6}\right).c_v.(T + \lambda\frac{dT}{dy})$

Similarly, the amount of heat flowing in the up ward direction from the layer EF that cross AB layer per unit area in unit time $Q_2 = \left(\frac{mn\bar{C}}{6}\right).c_v.(T - \lambda\frac{dT}{dy})$

The net flow of heat per unit area in unit time

$$Q = Q_1 - Q_2 = \left[\left(\frac{mn\bar{C}}{6}\right).c_v.(T + \lambda\frac{dT}{dy})\right] - \left[\left(\frac{mn\bar{C}}{6}\right).c_v.(T - \lambda\frac{dT}{dy})\right] = \frac{1}{6}.mn\bar{C}.\ c_v 2\lambda\frac{du}{dy}$$

$$\boxed{Q = \frac{1}{3}.mn\bar{C}.c_v\ \lambda\frac{du}{dy}} \longrightarrow (2)$$

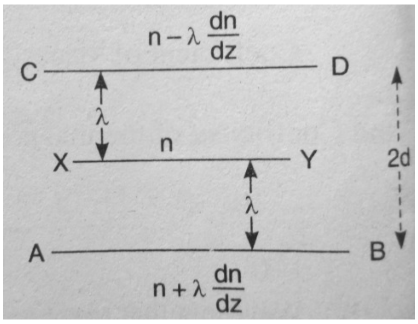
eqns. (1) & (2) are equal as they represent the quantity of heat flow.

$\therefore\ K\frac{dT}{dy} = \frac{1}{3}.mn\bar{C}.c_v\ \lambda\frac{dT}{dy}$ (or) $\boxed{K = \frac{1}{3}.mn\bar{C}.c_v\ \lambda = \frac{1}{3}.\rho\bar{C}.c_v\ \lambda}$

Here mn = ρ = density of gas

But $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$ $\quad\therefore$ $\boxed{K = \frac{1}{3}.mn\bar{C}.c_v\frac{1}{\sqrt{2}\pi d^2 n} = \frac{m\bar{C}c_v}{3\sqrt{2}\pi d^2}}$

Diffusion of gas



Consider a gas system as different layers parallel to x-axis. The concentration of gas in the layers increase as moved down. [Concentration is the no. of molecules per unit volume (n)]. Let ‘dn’ be the change in concentration between two layers separated by a distance ‘dz’. Then concentration gradient = $\frac{dn}{dz}$

If, A is the area through which molecules flow, then no. of molecules flow in time t, $N = D\frac{dn}{dz}.A.t$

Here D = Coefficient of diffusion.

$\boxed{N = D\frac{dn}{dz}} \longrightarrow$ (1) If the area is unity i.e. A = 1 & time is unity i.e. t =1

- ❖ Consider the gas layer XY having concentration ’n’. Take two more layers CD and AB, above & below XY layer, at a distance λ having concentrations $(n - \lambda\frac{dn}{dz})$ and $(n + \lambda\frac{dn}{dz})$ respectively. Here λ is mean free path.
- ❖ Average speed of molecules be $\bar{C}$. The molecules have velocity components in 6 directions. So, the no. of molecules moving in <u>one direction per unit area & per unit time</u> = $\frac{n\bar{C}}{6}$.
  The no. of molecules flowing in the down ward direction from the layer CD that cross XY layer per unit area in unit time $N_1 = \frac{\bar{C}}{6}.(n - \lambda\frac{dn}{dz})$

Similarly, the no. of molecules flowing in the up ward direction from the layer AB that cross XY layer per unit area in unit time $N_2 = \frac{\overline{C}}{6}.(n + \lambda\frac{dn}{dz})$

The net flow of no. of molecules per unit area in unit time

$$N = N_2 - N_1 = \left[\frac{\overline{C}}{6}.(n + \lambda\frac{dn}{dz})\right] - \left[\frac{\overline{C}}{6}.(n - \lambda\frac{dn}{dz})\right] = \frac{1}{6}.\overline{C}.\ 2\lambda\frac{dn}{dz}$$

$$\boxed{N = \frac{1}{3}.\overline{C}.\lambda\frac{dn}{dz}} \longrightarrow (2)$$

eqns. (1) & (2) are equal as they represent the quantity of no. of molecules flow.

$$\therefore D\frac{dn}{dz} = \frac{1}{3}.\overline{C}.\lambda\frac{dn}{dz} \quad \text{(or)} \quad \boxed{D = \frac{1}{3}.\overline{C}.\lambda}$$

But $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$ $\therefore$ $\boxed{K = \frac{1}{3}.\overline{C}.\frac{1}{\sqrt{2}\pi d^2 n} = \frac{\overline{C}}{3\sqrt{2}\pi d^2 n}}$

Relation between coefficient of viscosity & coefficient of thermal conductivity

We know that

Coefficient of viscosity $\eta = \frac{m\overline{C}}{3\sqrt{2}\pi d^2} \longrightarrow (1)$

Coefficient of thermal conductivity $K = \frac{m\overline{C}c_v}{3\sqrt{2}\pi d^2} \longrightarrow (2)$

Dividing the eqn. (2) by (1)

$$\frac{K}{\eta} = \frac{\frac{m\overline{C}c_v}{3\sqrt{2}\pi d^2}}{\frac{m\overline{C}}{3\sqrt{2}\pi d^2}} = c_v \quad \therefore \quad \boxed{\frac{K}{\eta} = c_v}$$

Relation between coefficient of viscosity & coefficient of diffusion of gas

We know that

Coefficient of viscosity $\eta = \frac{1}{3}.\rho\overline{C}.\lambda \longrightarrow (1)$

Coefficient of diffusion of gas $D = \frac{1}{3}.\overline{C}.\lambda \longrightarrow (2)$

Dividing the eqn. (1) by (2)

$$\frac{\eta}{D} = \frac{\frac{1}{3}.\rho\overline{C}.\lambda}{\frac{1}{3}.\overline{C}.\lambda} \quad \therefore \quad \boxed{\frac{\eta}{D} = \rho}$$

Formulae

1. $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$
2. $\eta = \frac{1}{3}.mn\overline{C}.\lambda = \frac{1}{3}.\rho\overline{C}.\lambda$
3. $\eta = \frac{1}{3}.mn\overline{C}.\frac{1}{\sqrt{2}\pi d^2 n} = \frac{m\overline{C}}{3\sqrt{2}\pi d^2}$
4. $K = \frac{1}{3}.mn\overline{C}.c_v\ \lambda = \frac{1}{3}.\rho\overline{C}.c_v\ \lambda$
5. $K = \frac{1}{3}.mn\overline{C}.c_v\ \frac{1}{\sqrt{2}\pi d^2 n} = \frac{m\overline{C}c_v}{3\sqrt{2}\pi d^2}$
6. $D = \frac{1}{3}.\ \overline{C}.\lambda$
7. $K = \frac{1}{3}.\ \overline{C}.\frac{1}{\sqrt{2}\pi d^2 n} = \frac{\overline{C}}{3\sqrt{2}\pi d^2 n}$
8. $\frac{K}{\eta} = c_v$
9. $\frac{\eta}{D} = \rho$
10. $C_p = \sqrt{2\ \frac{kT}{m}} = 1.414\sqrt{\frac{kT}{m}} = 1.414\sqrt{\frac{P}{\rho}} = 1.414\sqrt{\frac{RT}{M}}$
11. $\bar{C} = \sqrt{\frac{8}{\pi}\ \frac{kT}{m}} = 1.59\sqrt{\frac{kT}{m}} = 1.59\sqrt{\frac{P}{\rho}} = 1.59\sqrt{\frac{RT}{M}}$
12. $C_{rms} = \sqrt{3\ \frac{kT}{m}} = 1.732\sqrt{\frac{kT}{m}} = 1.732\sqrt{\frac{P}{\rho}} = 1.732\sqrt{\frac{RT}{M}}$
13. $\frac{kT}{m} = \frac{RT}{M}\quad i.e\ \frac{M}{m} = \frac{R}{K} = N\ Avegadro\ no. = \frac{Molecular\ wt.(M)}{Mass\ of\ molecule(m)}$

Chapter - II

Thermodynamics

Some definitions

1. Isothermal process :- If a system undergoes a physical change at constant temperature, then that change is called isothermal process.
2. Adiabatic process :- If a system under goes a physical change by keeping the amount of heat constant, then that change is called adiabatic process.
3. Isochoric process :- If a system under goes a physical change at constant volume, then that change is called isochoric process.
4. Isobaric process :- If a system under goes a physical change at constant pressure, then that change is called isobaric process.
5. Specific heat at constant volume (c_v):- It is the amount of heat required to rise the temperature of unit mass of gas through 1^0C at constant volume.
   S.I. unit is joule/Kg/ K (or) C.G.S unit is cal/gm/^{0}C
6. Specific heat at constant pressure (c_p) :- It is the amount of heat required to rise the temperature of unit mass of gas through 1^0C at constant pressure.
   S.I. unit is joule/Kg/ K (or) C.G.S unit is cal/gm/^{0}C
7. Heat capacity :- It is the amount of heat required to rise the temperature of the whole mass of the body through 1^0C.
   S.I. unit is joule/ K (or) C.G.S unit is cal/^{0}C
8. Molar specific heat at constant volume (C_V) :- It is the amount of heat required to rise the temperature of one mole of gas through 1^0C at constant volume.
   S.I. unit is joule/mol/ K (or) C.G.S unit is cal/mol/^{0}C
9. Molar specific heat at constant pressure (C_P) :- It is the amount of heat required to rise the temperature of one mole of gas through 1^0C at constant pressure.
   S.I. unit is joule/mol/ K (or) C.G.S unit is cal/mol/^{0}C
10. Zeroth law of thermodynamics :- If two bodies are separately in thermal equilibrium with a third body, then the first two bodies are also in thermal equilibrium.
    Explanation : - If two bodies A & B are in thermal equilibrium with a third body C, then A & B are also in thermal equilibrium.
    i.e. Let T_A, T_B & T_C are the temperatures of three bodies A B & C respectively.
    If $T_A = T_C$ and $T_B = T_C$ then $T_A = T_B$
11. Thermal equilibrium :- If the temperatures of two bodies are equal, then the two bodies are said to be in thermal equilibrium.
12. First law of thermodynamics :- The heat energy supplied to a system is equal to the sum of increase in internal energy and external work done.
    Explanation : - If dQ is the amount of heat given to a system, dU is the increase in the internal energy of the system and dW is the external work done by the system.

Then $dQ = dU + dW$ (or) $dQ = m\, c_v\, dT + P.dV = m\, c_p\, dT$

Here m = mass of the gas dT = increase in temperature dV = increase in volume P = pressure c_v = specific heat at constant volume c_p = specific heat at constant pressure

This is based on the law of conservation of energy.

13. Second law of thermodynamics :- It is not possible to transfer the heat from a body of lower temperature to a body of higher temperature with out the assistance of an external agency.

Distinction between isothermal and adiabatic processes

S.No.	**Isothermal process**	**Adiabatic process**
1.	If a system undergoes a physical change at constant temperature, then that change is called isothermal process.	If a system under goes a physical change by keeping the amount of heat constant, then that change is called adiabatic process
2.	In this process temperature is constant. i.e. T = constant or dT = 0	In this process the quantity of heat is constant. i.e. Q = constant or dQ = 0
3.	This process has heat exchange from surroundings.	This process has not any heat exchange from surroundings.
4.	The container is a good conductor.	Here the container is a bad conductor.
5.	This process is a slow process.	This process is a quick process.
6.	This obeys Boyle's law i.e. PV = constant	This obeys PV^{γ} = constant.

Applications of first law of thermodynamics

Isothermal process :- In isothermal process the temperature of the system is constant.

i.e. T = Constant (or) dT = 0. Then increase in internal energy dU = 0 as $dU = mc_v.\, dT$

As per the first law of thermodynamics $dQ = dU + dW$ (or) $dQ = 0 + P.dV$

$$dQ = P.dV$$

So, in this process the total heat given to the system is used to do external work. Similarly, work is done on the system, then an equal amount of heat is given out by the system.

Adiabatic process :- In adiabatic process the total energy of the system is constant.

i.e. Q = Constant (or) dQ = 0.

As per the first law of thermodynamics $dQ = dU + dW$ (or) $0 = dU + dW$

$$dU = -dW \text{ (or) } -dU = dW$$

So, in adiabatic compression, work is done on the system (- dW), then the internal energy increases (+dU) . Similarly, in adiabatic expansion, work is done by the system (+dW), then the internal energy decreases (-dU).

Adiabatic relations between pressure, volume & temperature for ideal gas

Temperature and volume

Consider 1 gram-mole of ideal gas (or) perfect gas having volume V, pressure P and temperature T, enclosed in a perfect insulating cylinder and piston. dV be the change in the volume of the gas in adiabatic process.

External work done by the gas system $\mathrm{dW} = \mathrm{P.dV}$

Decrease in the internal energy of the system $\mathrm{dU} = \mathrm{C_V.dT}$

Here C_V = molar specific heat at constant volume dT = change in temperature

As per 1st law of thermodynamics $\mathrm{dQ} = \mathrm{dU} + \mathrm{P.dV}$

$$0 = \mathrm{dU} + \mathrm{P.dV} \qquad \because \mathrm{dQ} = 0 \text{ in adiabatic process}$$

Substituting dU and dW in this equation $\mathrm{C_V.dT} + \mathrm{P.dV} = 0$

But for 1 gm-mol of ideal gas $PV = RT$ (or) $P = \frac{RT}{V}$

$$\therefore \mathrm{C_V.dT} + \frac{RT}{V}.\mathrm{dV} = 0 \quad \text{(or)} \quad \mathrm{C_V.dT} = -\frac{RT}{V}.\mathrm{dV}$$

$$\mathrm{C_V}.\frac{\mathrm{dT}}{T} = -R.\frac{\mathrm{dV}}{V}$$

Integrating on both sides $\int_{T_1}^{T_2} \mathrm{C_V}.\frac{\mathrm{dT}}{T} = -R\int_{V_1}^{V_2}\frac{\mathrm{dV}}{V}$

$$\mathrm{C_V}.\log_e\frac{T_2}{T_1} = -(\mathrm{C_P} - \mathrm{C_V}).\log_e\frac{V_2}{V_1}$$

$$\log_e\frac{T_2}{T_1} = \frac{(\mathrm{C_P} - \mathrm{C_V})}{\mathrm{C_V}}.\log_e\frac{V_1}{V_2}$$

$$\log_e\frac{T_2}{T_1} = (\gamma - 1).\log_e\frac{V_1}{V_2}$$

$$\log_e\frac{T_2}{T_1} = \log_e\left[\frac{V_1}{V_2}\right]^{(\gamma-1)}$$

(or) $$\frac{T_2}{T_1} = \left[\frac{V_1}{V_2}\right]^{(\gamma-1)} \longrightarrow (1)$$

(or) $$\boxed{T_1V_1^{(\gamma-1)} = T_2V_2^{(\gamma-1)}}$$

(or) $$\boxed{TV^{(\gamma-1)} = K}(constant)$$

Pressure and volume

From ideal gas equation $P_1\,V_1 = RT_1$ and $P_2\,V_2 = RT_2$

From these two equations $\frac{P_2\,V_2}{P_1\,V_1} = \frac{RT_2}{RT_1}$ (or) $\frac{P_2\,V_2}{P_1\,V_1} = \frac{T_2}{T_1} \longrightarrow$ (2)

Comparing the eqns. (1) & (2) $\frac{P_2\,V_2}{P_1\,V_1} = \left[\frac{V_1}{V_2}\right]^{(\gamma-1)}$

On cross multiplication $P_2\,V_2{}^{\gamma} = P_1\,V_1{}^{\gamma}$ (or) $\boxed{P\,V^{\gamma} = K}$ $(constant) \longrightarrow$ (3)

Pressure and temperature

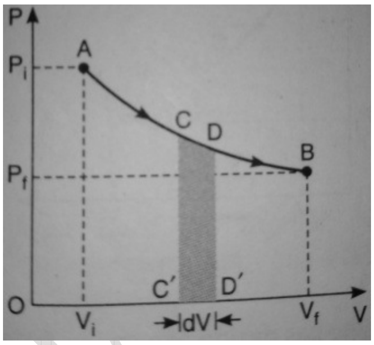
We know that PV = RT (or) $V = \frac{RT}{P} \longrightarrow$ (4)

Substituting eqn. (4) in (3) $p\,(\frac{RT}{P})^{\gamma} = K$ (or) $\boxed{P^{(1-\gamma)}T^{\gamma} = K}$ $(constant)$

Work done in isothermal process

Let 1 gram-mole of the gas is expanding isothermally. Let the initial pressure and volume be P_i & V_i and the final pressure and volume be P_f & V_f . The temperature T remains constant.

If the gas expands, the volume increases. Let the increase in volume be dV at pressure P.



Then work done $dW = P.dV$

But $PV = RT$ (or) $P = \frac{RT}{V}$

$$dW = RT\,\frac{dV}{V}$$

Then total work done $W = \int dW = \int_{V_i}^{V_f} RT\,\frac{dV}{V}$

$$\boxed{W = RT\,\log_e \frac{V_f}{V_i}}$$

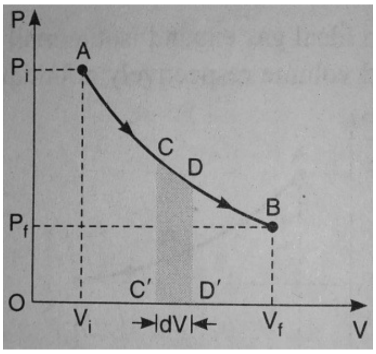
$$\boxed{W = 2.303\,x\,RT\,\log_{10} \frac{V_f}{V_i}}$$

This is the equation for work done in isothermal process.

Work done in adiabatic process

Let 1 gram-mole of the gas is expanding adiabatically. Let the initial pressure and volume be P_i & V_i and the final pressure and volume be P_f & V_f .

If the gas expands, the volume increases. Let the increase in volume be dV at pressure P.



Then work done $dW = P.dV$

In adiabatic process $PV^{\gamma} = K$ (or) $P = \frac{K}{V^{\gamma}}$

So, $dW = K\,\frac{dV}{V^{\gamma}}$

Total work done $W = \int dW = K \int_{V_i}^{V_f} \frac{dV}{V^{\gamma}} = K \int_{V_i}^{V_f} V^{-\gamma}\,dV$

$$W = \frac{K}{(1-\gamma)}\,[V^{(1-\gamma)}]_{V_i}^{V_f}$$

$$W = \frac{K}{(1-\gamma)}\,[{V_f}^{(1-\gamma)} - {V_i}^{(1-\gamma)}]$$

$$W = \frac{1}{(1-\gamma)}\,[K{V_f}^{(1-\gamma)} - K\,{V_i}^{(1-\gamma)}]$$

Put $K = P_i{V_i}^{\gamma} = P_f{V_f}^{\gamma}$

Then $W = \frac{1}{(1-\gamma)}\,[P_f{V_f}^{\gamma}.\,{V_f}^{(1-\gamma)} - P_i{V_i}^{\gamma}.{V_i}^{(1-\gamma)}]$

$$W = \frac{1}{(1-\gamma)}\,[P_fV_f - P_iV_i\,] \longrightarrow (1)$$

But as per ideal gas equation $P_fV_f = RT_f$ & $P_iV_i = RT_i \longrightarrow$ (2)

Substituting eqn. (2) in (1)

$$W = \frac{1}{(1-\gamma)}\,[RT_f - RT_i] \qquad \therefore \quad \boxed{W = \frac{R}{(1-\gamma)}\,[T_f - T_i]}$$

This is the equation for work done in adiabatic process.

Reversible process

Definition :- A reversible process is one which can be reversed at every point, in such a way that all changes occurring in direct process are exactly repeated in the opposite order and inverse sense and no changes are left in any of the bodies taking part in the process or in the surroundings.

Explanation:-

- ➢ If heat is absorbed in direct process, then the same amount of heat is given out in reverse process.
- ➢ If work is done on the working substance in direct process, then the same amount of work is done by the working substance in reverse process.

Conditions:-

- ✓ There should not be dissipative forces like friction, viscosity, electrical resistance etc.
- ✓ The direct and reverse processes must be very slow so that the system is always in equilibrium position.
- ✓ The temperatures of the system and surroundings must be very close to each other.

All these conditions are not possible in reality. So, reversible process is not possible and it is an ideal case.

Examples:-

1. All isothermal and adiabatic processes if they are performed very slowly.
2. Melting of ice:- when certain amount of heat is given to ice, then it melts in to water. If the same amount of heat is taken out the water is converted in to ice.
3. Very slow evapouration or condensation are also reversible.
4. When a perfectly elastic ball falls on a perfectly elastic surface in vacuum, then the ball raises to its initial height.
5. Very slow elongation or contraction of a spring without oscillatory motion is also reversible.

Irreversible process

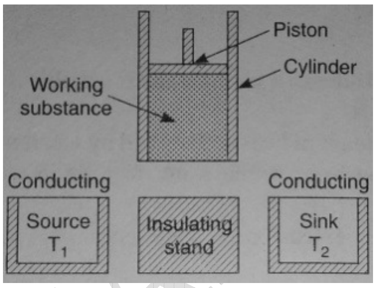
Definition :- An irreversible process is one which can not be reversed exactly in the opposite order.

Examples:-

1. Heat transfer from higher temperature body to lower temperature body is irreversible.
2. Heat produced in a resistor when current is passed through it is also irreversible process.
3. When an iron ball falls on plastic surface it can not raise to the initial height.
4. Joule-Thomson effect is irreversible process.
5. Vibrations in a stretched spring is irreversible.

Carnot's reversible engine

- Carnot's engine is theoretical heat engine and not practicable.
- Heat engine converts heat energy in to work.
- This has four parts.



1) Working substance :- Ideal gas is taken as working substance in cylinder-piston arrangement. The base of the cylinder is a perfect conductor of heat and all other faces of cylinder are made with perfect non-conducting material of heat. The piston is also non-conducting and frictionless.
2) Source of heat :- A hot body of very high thermal capacity is taken as source of heat. If any amount of heat is taken out from the source of high thermal capacity, its temperature does not fall. The source is maintained at high temperature T_1. The upper surface of source is good conductor of heat & all other faces are non-conductors.
3) Sink :- A cold body of very high thermal capacity is taken as sink. If any amount of heat is given to the sink of high thermal capacity, its temperature does not raise. The sink is maintained at low temperature T_2.(Generally, surrounding atmosphere is taken as sink). The upper surface of sink is good conductor of heat & all other faces are non-conductors.
4) Insulating stand :- To put the base of the cylinder for adiabatic process, a perfect non-conducting stand is taken.

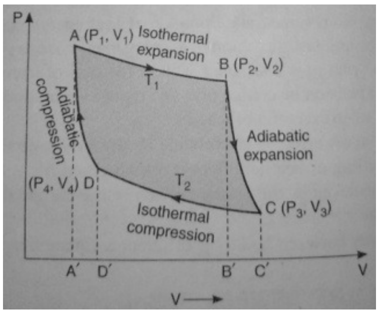
Carnot's cycle

In this the working substance is allowed to undergo a cyclic process and it has four parts.
Here 1 gm-mole of ideal gas is taken in the cylinder as working substance.

i. Isothermal expansion (A to B) :- Let A be the initial state of the substance in the indicator diagram and P_1, V_1,and T_1 be the pressure, volume and temperature of the substance respectively.

The cylinder is placed on the source at temperature T_1 and the gas is allowed to expand isothermally by taking heat Q_1 from the source. This is equal to the work done W_1 by the gas. Its temperature remains constant at T_1.

The final state of the gas is denoted by B and P_2, V_2,and T_1 be the pressure, volume and temperature of the substance respectively.



So, $Q_1 = W_1 = \int P.dV$

$$W_1 = \int_{V_1}^{V_2} RT_1 \frac{dV}{V} \qquad \because P\,V = R\,T_1\ (or)\ P = \frac{R\,T_1}{V}$$

$$W_1 = RT_1 \log_e \frac{V_2}{V_1} \longrightarrow (1)$$

(or) W_1 = Area ABB^1A^1A

ii. <u>Adiabatic expansion (B to C)</u> :- The cylinder is detached from the source and is placed on the insulated stand. The gas is allowed to expand adiabatically until it gets the temperature of the sink (T_2). Here the gas does some external work by using its internal energy. The final state of the gas is denoted by C and <u>P_3, V_3,and T_2</u> be the pressure, volume and temperature of the substance respectively.

In this adiabatic expansion, the work done $W_2 = \int P.dV$

$$W_2 = K \int_{V_2}^{V_3} \frac{dV}{V^\gamma} \qquad \because PV^\gamma = K \quad \text{(or)} \quad P = \frac{K}{V^\gamma}$$

$$W_2 = \frac{1}{(1-\gamma)}\left[k\, {V_3}^{1-\gamma} - k\, {V_2}^{1-\gamma}\right]$$

$$W_2 = \frac{1}{(1-\gamma)}\left[P_3{V_3}^\gamma\, {V_3}^{1-\gamma} - P_2{V_2}^\gamma\, {V_2}^{1-\gamma}\right] \qquad \because k = P_2{V_2}^\gamma = P_3{V_3}^\gamma$$

$$W_2 = \frac{1}{(1-\gamma)}\left[P_3V_3 - P_2V_2\right]$$

$$W_2 = \frac{1}{(1-\gamma)}\left[RT_2 - RT_1\right] \qquad \because P_3V_3 = RT_2 \,\&\, P_2V_2 = RT_1$$

$$W_2 = \frac{R}{(1-\gamma)}\left[T_2 - T_1\right] \longrightarrow (2)$$

(or) W_2 = Area $BC C^1 B^1 B$

iii. <u>Isothermal compression (C to D)</u> :- The cylinder is detached from the insulating stand and is placed on the sink at temperature (T_2). Now the gas is compressed isothermally. i.e. some work is done on the gas. Here the gas rejects an amount of heat Q_2 to the sink. The final state of the gas is denoted by D and <u>P_4, V_4,and T_2</u> be the pressure, volume and temperature of the substance respectively.

So, $Q_2 = W_3 = \int P.dV$

$$W_3 = \int_{V_3}^{V_4} RT_2 \frac{dV}{V} \qquad \because P\,V = R\,T_2\ (or)\ P = \frac{R\,T_2}{V}$$

$$W_3 = RT_2 \log_e \frac{V_4}{V_3} \longrightarrow (3)$$

(or) W_3 = Area $CD D^1 C^1 C$

iv. <u>Adiabatic compression (D to A)</u> :- In this process the cylinder is detached from the sink and placed on the insulating stand. The gas is compressed adiabatically until it goes to the initial state A. Here also some work is done on the gas. If W_4 is the work done. Then, it can be drawn as eqn.(2)

$$W_4 = \frac{R}{(1-\gamma)}\left[T_1 - T_2\right] \longrightarrow (4)$$

(or) W_4 = Area $DA A^1 D^1 D$

<u>Efficiency of the engine</u>

$$Efficiency\ of\ the\ engine\ (\eta) = \frac{Work\ done\ by\ the\ engine}{Heat\ taken\ from\ the\ source} = \frac{Heat\ converted\ into\ work}{Heat\ taken\ from\ the\ source}$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \longrightarrow (5)$$

Net work done by the gas $W = W_1 + W_2 + W_3 + W_4$

Substituting W_1, W_2, W_3 & W_4 values in the above equation

$$W = RT_1 \log_e \frac{V_2}{V_1} + \frac{R}{(1-\gamma)} [T_2 - T_1] + RT_2 \log_e \frac{V_4}{V_3} + \frac{R}{(1-\gamma)} [T_1 - T_2]$$

$$W = RT_1 \log_e \frac{V_2}{V_1} + RT_2 \log_e \frac{V_4}{V_3} \longrightarrow (6)$$

Points B & C are on the same adiabatic expansion.

So, $T_1 V_2^{(\gamma-1)} = T_2 V_3^{(\gamma-1)}$ (or) $\frac{T_1}{T_2} = \left[\frac{V_3}{V_2}\right]^{(\gamma-1)} \longrightarrow$ (7)

Similarly, Points D & A are on the same adiabatic contraction.

So, $T_2 V_4^{(\gamma-1)} = T_1 V_1^{(\gamma-1)}$ (or) $\frac{T_1}{T_2} = \left[\frac{V_4}{V_1}\right]^{(\gamma-1)} \longrightarrow$ (8)

Comparing eqns. (7) & (8) $\frac{V_3}{V_2} = \frac{V_4}{V_1}$ (or) $\frac{V_4}{V_3} = \frac{V_1}{V_2} \longrightarrow$ (9)

Substituting eqn. (9) in (6) $W = RT_1 \log_e \frac{V_2}{V_1} + RT_2 \log_e \frac{V_1}{V_2}$

$$W = R\,(T_1 - T_2) \log_e \frac{V_2}{V_1} \longrightarrow (10)$$

Substituting eqns. (10) & (1) in (5) $\eta = \frac{W}{Q_1} = \frac{R\,(T_1 - T_2) \log_e \frac{V_2}{V_1}}{RT_1 \log_e \frac{V_2}{V_1}}$

$$\eta = \frac{(T_1 - T_2)}{T_1} \quad \text{(or)} \quad \boxed{\eta = \left(1 - \frac{T_2}{T_1}\right)}$$

Impracticability of Carnot's engine

1. In real, when heat is taken from the source, its temperature falls and similarly when heat is given to the sink its temperature raises. So, heat can not be taken or rejected strictly at constant temperatures.
2. Preparing the cylinder of engine having base with perfect conducting material and other parts with perfect non-conducting material is also not possible.
3. If the engine works very slowly, it can not be used in day to day life even though the efficiency is high.
4. In reverse cycle, the working substance should take the heat (Q_2) from the sink at low temperature (T_2) and give the heat (Q_1) to source at high temperature(T_1). This is the working of refrigerator. This is also not possible with out the help of external aid.

Hence, Carnot's engine is impracticable and it is an ideal engine.

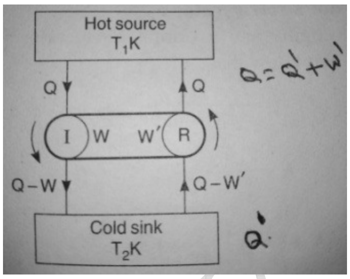
Carnot's theorem

Statement:- No engine is more efficient than reversible engine working between the same two temperatures. (or)

All reversible engines working between same two temperatures have the same efficiency, what ever the working substance it may be.

Proof:-

- Consider a reversible engine R and an irreversible engine I working between the same source and sink.



- I works in forward direction and R works in back ward direction.
- Let the Q be the energy absorbed by the engine I from the source at T_1. This engine converts some energy into work W and the remaining energy (Q-W) is transferred to the sink at T_2.
- Similarly, Q^1 be the energy absorbed by the engine R from the sink at T_2. W^1 is the work done on the substance. The energy transferred to the source is (Q^1+W^1).
- Let the source gives and takes the same amount of energy

  i.e. $Q = Q^1+W^1$ (or) $W^1 = Q - Q^1$

  Also assume that efficiency of irreversible engine I > efficiency of reversible engine R

  $$\eta_I > \eta_R$$

  $$\frac{W}{Q} > \frac{W^1}{Q} \quad \text{i.e.} \quad W > W^1 \longrightarrow (1)$$

  Now couple the two engines

  In compound engine the sink takes the heat (Q-W) and gives the heat $(Q-W^1)$

  So, the net amount of heat given by the sink $= (Q-W^1) - (Q-W) = W - W^1 \longrightarrow$ (2)

  As per eqn. (1), eqn. (2) is positive. Then $(Q-W^1) > (Q-W)$

  This means that the sink takes less heat (Q-W) and gives more heat $(Q-W^1)$ with out any change in the sink. This is impossible as per the second law of thermodynamics. So, eqn. (2) as well as eqn. (1) are wrong.

  Hence, the efficiency of reversible engine is greater than the efficiency if irreversible engine. $i.e.\quad \eta_R > \eta_I$

  <u>Proof for the 2nd part</u> :-

- ✪ Consider <u>two reversible engines X and Y</u> working between the same source and sink.
- ✪ If X drives Y in back word direction then X is not more efficient than Y.
- ✪ Similarly, if Y drives X in the back ward direction then Y is not more efficient than X.
- ✪ From the above two statements it is clear that the two reversible engines have the same efficiency.
- ✪ So, all reversible engines working between same two temperatures have the same efficiency & the efficiency does not depend on the working substance.

Second law of thermodynamics

Kelvin statement of second law :- It is impossible to draw continuous supply of work by cooling a body below the temperature of surroundings.

Clausius statement of second law :- It is impossible to transfer heat from a cold body to a hot body with out the assistance of an external agency.

Kelvin scale of temperature :-It is the scale in which the ratio of any two temperatures is equal to the ratio of the heats absorbed and rejected by reversible Carnot's engine operating between the these temperatures.

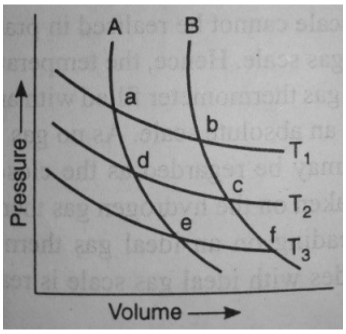
Explanation : - Let Q_1 be the heat absorbed from the source at temperature T_1 and Q_2 be the heat rejected at sink at temperature T_2.

Then $\boxed{\frac{T_1}{T_1} = \frac{Q_1}{Q_2}}$

Entropy

- In adiabatic compression work is done on the gas then heat and temperature both increase.
- Similarly, in adiabatic expansion work is done by the gas then the heat and temperature both decrease.
- So, in adiabatic process neither the heat nor the temperature remains constant.
- Clausius explained entropy which is constant in adiabatic process.

Def:- The physical quantity that remains constant in adiabatic process is called entropy.



Explanation :- Consider different isothermal processes at temperatures T_1, T_2, T_3 …. etc and two adiabatic processes A &B. The adiabatics intercept the isothermals at points a, b, c, d, e &f as shown in figure.

Take the reversible Carnot's cycle along abcda between temperatures T_1& T_2. Let Q_1 be the heat taken at T_1 & Q_2 be the heat rejected at T_2 (adiabatic process from b to c).

Then $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ (or) $\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \longrightarrow (1)$

If, the reversible Carnot's cycle along dcfed is taken between temperatures T_2& T_3 . Let Q_2 be the heat taken at T_2 & Q_3 be the heat rejected at T_3 (adiabatic process from c to f).

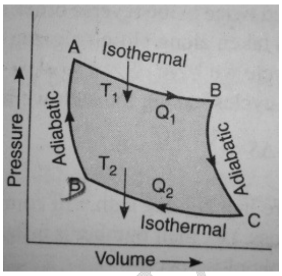
Then $\frac{Q_2}{Q_3} = \frac{T_2}{T_3}$ (or) $\frac{Q_2}{T_2} = \frac{Q_3}{T_3} \longrightarrow (2)$

From eqns. (1) & (2) $\boxed{\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3}}$ (or) $\boxed{\frac{Q}{T} = Constant}$ in adiabatic process

- Measurement of absolute entropy is not possible. So, change of entropy is measured.

  So, change of entropy $\boxed{dS = \frac{dQ}{T}}$
- Change of entropy between two states does not depend on the path but depends on the states only.
- Entropy is also a physical quantity like pressure and volume.

Change in entropy in reversible cycle



Consider the change of entropy for the substance taking reversible Carnot's cycle ABCD. Let the initial state is A.

Q_1 be the heat taken by the substance for its isothermal expansion AB at temperature T_1.

Change in entropy $dS_1 = \frac{Q_1}{T_1}$

In adiabatic expansion BC, no change in heat. Change in entropy $dS_2 = 0$

Q_2 be the heat rejected by the substance for its isothermal compression CD at temperature T_2.

Change in entropy $dS_3 = -\frac{Q_2}{T_2}$

In adiabatic compression DA, no change in heat. Change in entropy $dS_4 = 0$

The net change in entropy for the complete cycle is $dS = dS_1 + dS_2 + dS_3 + dS_4$

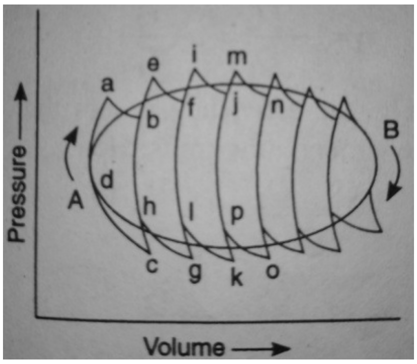
$$dS = \frac{Q_1}{T_1} + 0 - \frac{Q_2}{T_2} + 0$$

But from the Kelvin scale temperature $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$

So dS = 0

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

Consider a general case of reversible cycle ABA.



This cycle is divided into so many number of Carnot's cycles. These cycles are a b c d, e f g h, i j k l etc.

The sum of the change of entropy of all Carnot's cycles

$dS = \sum \frac{dQ}{T} = 0$

The paths b h, f l, j p, etc cancel out because these paths are traversed twice in reverse order. But the zig – zag path a b e f i .. .. g h c a only remains. If the adiabatics are very close then this zig-zag paths coincides with A B A path and also the no. of adiabatics become infinite. Then the sum is replaced by an integral.

$$\therefore \quad \boxed{dS = \int \frac{dQ}{T} = 0}$$

So, the net change in entropy for any reversible cycle is zero.

Change in entropy in irreversible cycle

Consider a irreversible cycle. Let Q_1 be the heat absorbed at temperature T_1 and Q_2 be the heat rejected at temperature T_2.

Efficiency of irreversible cycle $\eta_I = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

Efficiency of reversible Carnot,s cycle $\eta_R = 1 - \frac{T_2}{T_1}$

As per Carnot's theorem $\eta_I < \eta_R$

i.e. $1-\frac{Q_2}{Q_1} < 1-\frac{T_2}{T_1}$ (or) $\frac{Q_2}{Q_1} > \frac{T_2}{T_1}$ (or) $\frac{Q_2}{T_2} > \frac{Q_1}{T_1}$

So, the entropy increases in all irreversible processes.

Entropy and disorder

- If a matter is in solid state the molecules are arranged in orderly manner. Their motion is restricted due to intermolecular forces. The disorder is some what less and it has some entropy.
- When the solid is converted into liquid the entropy value increases. Then the degree of freedom of molecules increases and the orderliness decreases or the disorder increases.
- When the liquid is converted in to gaseous state its entropy increases and the molecules will get high degree of freedom and these molecules can move randomly through out the system with out any restriction. Their position can not be specified , it means their disorder further increases.
- From the above discussion it is clear that when entropy increases the motion of molecules changes from order to disorder. The converse is also true.
- So, the measurement of disorder is entropy.

Free expansion :- Consider two vessels A & B. A is filled with gas and B is empty. These two are connected by a stop-cock. When the stop-cock is suddenly opened the gas molecules from A spread into B. The distribution of molecules in B is more random than when they were in A. But in free expansion the entropy increases. So, here also the disorder increases along with entropy.

Entropy of universe

- ⊙ In reversible cycle the entropy remains constant but in irreversible cycle the entropy increases.
- ⊙ All the natural processes in the universe are irreversible. So, the entropy of the universe increases (or) the available energy (useful to do work) decreases.

In a Carnot's engine Q_1 be the heat taken from the hot body at temperature T_1 and Q_2 be the heat given to the cold body at temperature T_2. Here (Q_1- Q_2) is the heat energy converted in to work and is called available energy.

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

$$= Q_1\left(1-\frac{T_2}{T_1}\right) \qquad \because \frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

If T_2 is decreased then the available energy increases.

Let T_0 be the lowest temperature in a irreversible system of heat conduction and Q be the quantity of heat transferred from a hot body at temperature T_1 to a cold body at temperature T_2.

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

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

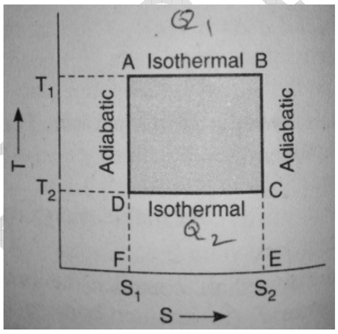
$$\text{Loss of available energy} = Q\left(1-\frac{T_0}{T_1}\right) - Q\left(1-\frac{T_0}{T_2}\right) = Q\left(\frac{T_0}{T_2}-\frac{T_0}{T_1}\right)$$

$= T_0\left(\frac{Q}{T_2} - \frac{Q}{T_1}\right) = T_0 ds$ Here dS is the change in entropy.

The above eqn. says that the entropy is increasing in irreversible process or in universe.

As per law of conservation of energy the energy of the universe is constant but the entropy or the disorder is increasing and the available energy is decreasing or tending towards zero.

Temperature and entropy diagram



The graph drawn by taking temperature (T) on Y – axis and entropy (S) on X – axis is called temperature and entropy diagram (or) T-S diagram.

In isothermal process the temperature T is constant and in adiabatic process the entropy S is constant. So, for reversible cycle the T-S diagram is more useful than P-V diagram.

- Consider the Carnot's cycle, in this, the first stage is isothermal expansion & is represented by AB, here the working substance takes heat Q_1 from the source at constant temperature T_1 and the entropy increases from S_1 to S_2.

$$Q_1 = T_1(S_2 - S_1) = AFxAB$$
$$Q_1 = Area\ of\ \ ABEF \longrightarrow (1)$$

- In the second stage adiabatic expansion takes place on the insulated stand, this is represented by BC. Here the temperature falls from T_1 to T_2. No change in entropy (Area is zero).
- In the third stage isothermal compression takes place & is represented by CD. Here the working substance gives out heat Q_2 to the sink at constant temperature T_2 and the entropy decreases from S_2 to S_1.

$$Q_2 = T_2(S_2 - S_1) = DFxDC$$
$$Q_2 = Area\ of\ \ DCEF \longrightarrow (2)$$

- In the fourth stage adiabatic compression takes place on the insulated stand, this is represented by DA. Here the temperature rises from T_2 to T_1. No change in entropy (Area is zero).

Available energy or amount of heat converted in to work

$$W = Q_1 - Q_2$$
$$W = Area\ of\ \ ABEF - Area\ of\ \ DCEF$$
$$W = Area\ of\ \ ABCD$$

This is the area of the T-S diagram.

Similarly, the efficiency $\eta = \frac{W}{Q_1} = \frac{Area\ of\ \ ABCD}{Area\ of\ \ ABEF}$

$$\eta = \frac{AB\ x\ AD}{AB\ x\ AF} = \frac{AD}{AF}$$

$$\eta = \frac{T_1 - T_2}{T_1} \quad \text{(or)} \quad \boxed{\eta = 1 - \frac{T_2}{T_1}}$$

Entropy of perfect gas

Consider 1 gm-mol of perfect gas at pressure P, temperature T and having the volume V. Let dQ be the heat given to the gas.

Then, increase in entropy $dS = \frac{dQ}{T}$

From 1st law of thermodynamics dQ = dU + dW

$$dQ = C_v dT + P\,dV \qquad C_v = Molar\ sp.heat\ at\ constant\ volume$$

$$dS = \frac{C_v dT}{T} + \frac{P\,dV}{T} \longrightarrow (1)$$

I. To express the entropy S in terms of T & V, eliminate P in eqn. (1) by substituting $P = \frac{RT}{V}$

$$dS = \frac{C_v dT}{T} + \frac{RT}{V}\frac{dV}{T} = C_v\frac{dT}{T} + R\frac{dV}{V}$$

Let S_f, S_i, T_f, T_i, V_f, V_i are final and initial values of entropy, temperature and volume respectively.

Integrating the above equation

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

$$\boxed{(S_f - S_i) = 2.303\left[C_v \log_{10}\left(\frac{T_f}{T_i}\right) + R\log_{10}\left(\frac{V_f}{V_i}\right)\right]} \longrightarrow (i)$$

II. To express the entropy S in terms of T & P, eliminate dV and then V in eqn. (1)

For ideal gas PV = RT

P.dV + V. dP = R dT (or) $dV = \frac{R.dT - V.dP}{P}$

Substituting dV value in eqn. (1)

$$dS = \frac{C_v dT}{T} + \frac{P}{T}\,\frac{R.dT - V.dP}{P} = \frac{C_v dT}{T} + \frac{R.dT - V.dP}{T}$$

$$dS = \frac{C_v dT}{T} + R.\frac{dT}{T} - V.\frac{dP}{T}$$

$$dS = (C_v + R)\frac{dT}{T} - V.\frac{dP}{T}$$

But $(C_v + R) = C_p$ and $V = \frac{RT}{P}$

Substituting these two values $dS = C_p\frac{dT}{T} - \frac{RT}{P}.\frac{dP}{T}$ (or) $dS = C_p\frac{dT}{T} - R.\frac{dP}{P}$

Let S_f, S_i, T_f, T_i, P_f, P_i are final and initial values of entropy, temperature and pressure respectively.

Integrating the above equation

$$\int_{S_i}^{S_f} dS = C_p\int_{T_i}^{T_f}\frac{dT}{T} - R\int_{P_i}^{P_f}\frac{dP}{P}$$

$$\boxed{(S_f - S_i) = 2.303\left[C_p \log_{10}\left(\frac{T_f}{T_i}\right) - R\log_{10}\left(\frac{P_f}{P_i}\right)\right]} \longrightarrow (ii)$$

III. To express the entropy S in terms of P & V, eliminate dT and then T in eqn. (1)

For ideal gas $PV = RT$

$$P.dV + V.dP = R\,dT \qquad \text{(or)}\ dT = \frac{P.dV + V.dP}{R}$$

$$dS = \frac{C_v}{T}\frac{P.dV + V.dP}{R} + \frac{P\,dV}{T} = C_v\frac{P.dV + V.dP}{RT} + \frac{P\,dV}{T}$$

Substitute $T = \frac{PV}{R}$ in the above equation

$$dS = C_v\frac{P.dV + V.dP}{R\frac{PV}{R}} + \frac{P\,dV}{\frac{PV}{R}}$$

$$dS = C_v\frac{P.dV + V.dP}{PV} + R\frac{dV}{V}$$

$$dS = C_v\frac{dV}{V} + C_v\frac{dP}{P} + R\frac{dV}{V}$$

$$dS = (C_v + R)\frac{dV}{V} + C_v\frac{dP}{P}$$

$$dS = C_p\frac{dV}{V} + C_v\frac{dP}{P} \qquad \because (C_v + R) = C_p$$

Let S_f, S_i, V_f, V_i, P_f, P_i are final and initial values of entropy, volume and pressure respectively.

Integrating the above equation

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

$$\boxed{\left(S_f - S_i\right) = 2.303\left[C_p\log_{10}\left(\frac{V_f}{V_i}\right) + C_v\log_{10}\left(\frac{P_f}{P_i}\right)\right]} \longrightarrow \text{(iii)}$$

Change of entropy for a perfect gas can be calculated by using any one of the three equations (i), (ii) & (iii) depending on the given data.

Change of entropy in isothermal process

$$\left(S_f - S_i\right) = 2.303\,R\,\log_{10}\left(\frac{V_f}{V_i}\right)$$

Or
$$\left(S_f - S_i\right) = -2.303\,R\,\log_{10}\left(\frac{P_f}{P_i}\right)$$

Change of entropy in isochoric process

$$\left(S_f - S_i\right) = 2.303\,C_v\log_{10}\left(\frac{T_f}{T_i}\right)$$

(or)
$$\left(S_f - S_i\right) = 2.303\,C_v\log_{10}\left(\frac{P_f}{P_i}\right)$$

Change of entropy in isobaric process

$$\left(S_f - S_i\right) = 2.303\,C_p\log_{10}\left(\frac{T_f}{T_i}\right)$$

(or)
$$\left(S_f - S_i\right) = 2.303\,C_p\log_{10}\left(\frac{V_f}{V_i}\right)$$

Change of entropy when ice changes in to steam

Let m be the mass of the ice at temperature T_1 is converted in to steam of temperature T_2. Let s be the specific heat of water, L_1 be the latent of fusion of ice and L_2 be the latent heat of vapourisation.

The general equation for entropy $dS = \frac{dQ}{T}$

- ✓ Change of entropy when m mass of ice at T_1 is converted in to water at T_1.

$$dS_1 = \frac{mL_1}{T_1} \longrightarrow (1)$$

- ✓ Change of entropy when m mass of water at T_1 is changed in to water at T_2.

$$dS_2 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{ms\, dT}{T}$$

$$dS_2 = ms \log_e(\frac{T_2}{T_1}) = 2.303\, ms \log_{10}(\frac{T_2}{T_1}) \longrightarrow (2)$$

- ✓ Change of entropy when m mass of water at T_2 is converted in to steam at T_2.

$$dS_3 = \frac{mL_2}{T_2} \longrightarrow (3)$$

Total change of entropy when ice changes in to steam $dS = dS_1 + dS_2 + dS_3 \longrightarrow (4)$

Substituting eqns. (1), (2) & (3) in eqn. (4)

Then, the total change of entropy $\boxed{dS = \frac{mL_1}{T_1} + 2.303\, ms \log_{10}(\frac{T_2}{T_1}) + \frac{mL_2}{T_2}}$

Chapter - III

Thermodynamic Potentials and Maxwell's Equations

Thermodynamic Potentials

- ✪ To describe the thermodynamic state of a system completely, more relations are required other than basic thermodynamic variables, pressure(P), volume(V), temperature(T) and entropy(S).
- ✪ Definition:- The energy functions formed by combining the basic thermodynamic variables are called thermodynamic potentials.
- ✪ In basic thermodynamic variables, two are independent and the rest are dependent.
- ✪ The four thermodynamic potentials are i) Internal Energy(U) ii) Helmholtz function(F) iii) Enthalpy or Total heat function(H) and iv) Gibb's function(G).
- ✪ A conservative mechanical system is in equilibrium when the potential energy of the system is minimum. Similarly, the thermodynamic system is in equilibrium when the thermodynamic potentials values are minimum.

From 1st law of thermodynamics $dQ = dU + dW = dU + P.dV$

From 2nd law of thermodynamics $dQ = T.dS$

Combining the two equations $T.dS = dU + P.dV$

(or) $$\boxed{dU = T.dS - P.dV} \longrightarrow (1)$$

This is the basic equation that connects 1st & 2nd laws of thermodynamics.

I. **Internal Energy(U)** :-

- ◈ The internal energy of a system is the sum of potential energy and kinetic energy.
- ◈ The potential energy is due to mutual attraction among the molecules and the kinetic energy is due to the motion of the molecules.
- ◈ If the system changes from one state to the other, then the change in the internal energy does not depend on the path but it depends on the initial and final states only.

From 1st & 2nd laws of thermodynamics, we know that $dU = T.dS - P.dV$

Taking the partial differentiation for the above eqn. with respect to independent variables S and V.

$$\left(\frac{\partial U}{\partial s}\right)_V = T \quad and \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \longrightarrow (2)$$

These are the relations connecting U and P, V, T & S.

As dU is a perfect differential $$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial s}\right)_V = \frac{\partial}{\partial s}\left(\frac{\partial U}{\partial V}\right)_S \longrightarrow (3)$$

Substituting eqn. (2) in (3) $$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

This is the Maxwell's 1st thermodynamic relation.

II. **Helmholtz function (F)** :-

From 1st & 2nd laws of thermodynamics, we know that $dU = T.dS - P.dV$

Consider the system is isothermal. Then T = Constant

$$T.\,dS = d(TS)$$

$$dU = d(TS) - P.dV \quad \text{(or)} \quad dU - d(TS) = -P.dV$$

$$d(U - TS) = -P.dV$$

Put $U - TS = F$ (or) $\boxed{F = U - TS} \longrightarrow (4)$

This is called Helmholtz free energy or work function.

Then $dF = -P.dV = -dW$

i.e. The external work done on the system is equal to change in Helmholtz function.

From eqn. (4) the change in the Helmholtz function $dF = dU - T\,dS - S\,dT$

But $dU = T.dS - P.dV$

$$Then \quad dF = (T.dS - P.dV) - T\,dS - S\,dT$$

$$\therefore \quad dF = -P.dV - S\,dT$$

Taking the partial differentiation for the above eqn. with respect to independent variables T and V.

$$\left(\frac{\partial F}{\partial V}\right)_T = -P \quad and \quad \left(\frac{\partial F}{\partial T}\right)_V = -S \longrightarrow (5)$$

These are the relations connecting F and P, V, T & S.

As dF is a perfect differential $\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T \longrightarrow (6)$

Substituting eqn. (5) in (6) $\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$

This is the Maxwell's 2nd thermodynamic relation.

III. **Enthalpy (or) Total heat function (H)** :-

Enthalpy is heat function at constant pressure like internal energy at constant volume.

This can be written as $\boxed{H = U + PV}$

On differentiation $dH = dU + P.dV + V.dP$

But $dU = T.dS - P.dV$

Then $dH = (T.dS - P.dV) + P.dV + V.dP$

$$\therefore \quad dH = T.dS + V.dP$$

Taking the partial differentiation for the above eqn. with respect to independent variables S and P.

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad and \quad \left(\frac{\partial H}{\partial P}\right)_S = V \longrightarrow (7)$$

These are the relations connecting H and P, V, T & S.

As dH is a perfect differential $\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S \longrightarrow (8)$

Substituting eqn. (7) in (8) $\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$

This is the Maxwell's 3rd thermodynamic relation.

IV. **Gibb's function(G)** :-

From the definition of enthalpy $H = U + PV$

On differentiation $dH = dU + P.dV + V.dP$

But $dU = T.dS - P.dV$

Then $dH = (T.dS - P.dV) + P.dV + V.dP$

$\therefore\ dH = T.dS + V.dP$

If the system is isothermal. Then T = Constant

$T.dS = d(TS)$

If the system is isobaric. Then P = Constant & dP = 0

Then $dH = d(TS) + 0$ (or) $dH - d(TS) = 0$

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

This is called Gibb's function.

$\therefore\ \boxed{G = H - TS}$

Gibb's function remains constant if the thermodynamic process is isothermal as well as isobaric.

On differentiation $dG = dH - T.dS - S.dT$

But $dH = T.dS + V.dP$

So, $dG = (T.dS + V.dP) - T.dS - S.dT$

$\therefore\ dG = V.dP - S.dT$

Taking the partial differentiation for the above eqn. with respect to independent variables P and T.

$$\left(\frac{\partial G}{\partial P}\right)_T = V \quad and \quad \left(\frac{\partial G}{\partial T}\right)_P = -S \longrightarrow (9)$$

These are the relations connecting G and P, V, T & S.

As dG is a perfect differential $\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P \longrightarrow (10)$

Substituting eqn. (9) in (10) $\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$

This is the Maxwell's 4th thermodynamic relation.

These four Maxwell's thermodynamic relations are derived from thermodynamic potentials.

Note :- U is a function of independent variables S & V.
F is a function of independent variables T & V.
H is a function of independent variables S & P.
G is a function of independent variables P & T.

Maxwell's thermodynamic relations

Here the Maxwell's thermodynamic relations will be derived from the laws of thermodynamics.

From 1st law of thermodynamics $dQ = dU + dW = dU + P.dV$

From 2nd law of thermodynamics $dQ = T.dS$

Combining the two equations $T.dS = dU + P.dV$

$$\text{(or)} \quad \boxed{dU = T.dS - P.dV} \longrightarrow \quad (1)$$

This is the basic equation that connects 1st & 2nd laws of thermodynamics.

Let x & y be the any two independent variables out of four P, V, T, & S.

Let U, S &V are functions of x and y.

$$\left.\begin{aligned} dU &= \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy \\ dS &= \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \\ dV &= \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \end{aligned}\right\} \longrightarrow \quad (2)$$

Substituting equation (2) i.e (du, dS & dV values) in (1)

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

x & y are independent variables. Comparing the coefficients of dx & dy on both sides.

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \longrightarrow \quad (3)$$

$$\text{And} \quad \left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \longrightarrow \quad (4)$$

Differentiating eqn. (3) with respect to y & differentiating eqn. (4) with respect to x.

$$\frac{\partial^2 U}{\partial y.\partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y.\partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y.\partial x} \longrightarrow \quad (5)$$

$$\frac{\partial^2 U}{\partial x.\partial y} = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x.\partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x.\partial y} \longrightarrow \quad (6)$$

Here dU, dS & dV are perfect differentials, so the order of differentiation does not make any difference. i.e. first differentiating with respect to x and then with respect to y is same as, first differentiating with respect to y and then with respect to x.

$$\text{So,} \quad \frac{\partial^2 U}{\partial y.\partial x} = \frac{\partial^2 U}{\partial x.\partial y}, \quad \frac{\partial^2 S}{\partial y.\partial x} = \frac{\partial^2 S}{\partial x.\partial y} \quad \& \quad \frac{\partial^2 V}{\partial y.\partial x} = \frac{\partial^2 V}{\partial x.\partial y} \longrightarrow \quad (7)$$

Eqns. (5) & (6) are equal as per the eqn. (7)

On equating the eqns. (5) & (6) & cancelling the equal terms

$$\boxed{\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x} \longrightarrow \quad (8)$$

This is the general Maxwell's thermodynamic relation.

First relation:- Put x = S and y = V

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

Substituting these values in eqn. (8)

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

This is the Maxwell's 1st thermodynamic relation

Second relation:- Put x = T and y = V

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

Substituting these values in eqn. (8) $0 = \left(\frac{\partial S}{\partial V}\right)_T - \left(\frac{\partial P}{\partial T}\right)_V$

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

This is the Maxwell's 2nd thermodynamic relation.

Third relation:- Put x = S and y = P

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

Substituting these values in eqn. (8) $\left(\frac{\partial T}{\partial P}\right)_S - \left(\frac{\partial V}{\partial S}\right)_P = 0$

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

This is the Maxwell's 3rd thermodynamic relation.

Fourth relation:- Put x = T and y = P

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

Substituting these values in eqn. (8) $\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T}$

This is the Maxwell's 4th thermodynamic relation.

Applications of Maxwell's thermodynamic relations

Clausius-Clapeyron equation (Based on Maxwell's equations)

- The Clasius-Clapeyron latent heat equation gives the relation between the change in melting point (or) boiling point and change in pressure.
- This equation can be derived by using the Maxwell's 2nd thermodynamic relation.

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

Multiplying both sides by T

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

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial V}\right)_T \longrightarrow (1) \qquad \because\ T\partial S = \partial Q \text{ from 2nd law of thermodynamics}$$

Consider the unit mass of substance that is converted from one state to the other.

Change in the volume $\partial V = (v_2 - v_1)$

v_1 & v_2 $are\ the\ initial\ and\ final\ specific\ volumes$ (volume per unit mass).

$$\partial Q = Heat\ absorbed\ per\ unit\ mass\ at\ constant\ temperature = Latent\ heat = L$$

Substituting ∂Q and ∂V values in eqn. (1)

$$T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{L}{v_2 - v_1}\right)_T \quad \text{(or)} \quad \boxed{\frac{\partial P}{\partial T} = \frac{L}{T(v_2 - v_1)}}$$

This is the Clasius - Clapeyron latent heat equation.

Applications of Clasius-Clapeyron latent heat equation:-

1) If the volume increases when liquid is converted in to gas i.e. ($v_2 > v_1$) then ($v_2 - v_1$) is positive and $\frac{\partial P}{\partial T}$ becomes positive. This means that both ∂P & ∂T will become positive (or) both will become negative. i.e. The boiling point increases with increase of pressure and vice versa.
2) In case of melting point i.e. when solid is converted into liquid two cases will arise.

   Case 1 :- When $v_2 > v_1$, then ($v_2 - v_1$) is positive and $\frac{\partial P}{\partial T}$ becomes positive. Here the melting point increases with increase of pressure and vice versa. Ex: Wax & Sulpher

   Case 2 :- When $v_2 < v_1$, then ($v_2 - v_1$) is negative and $\frac{\partial P}{\partial T}$ becomes negative. This means that either ∂P *or* ∂T will become positive and the other term becomes negative. Then the melting point increases with degrease of pressure and vice versa. Ex:Bismuth, Gallium & Ice.
3) Regelation of Ice :- When two Ice blocks are pressed together the pressure on the two surfaces of contact increases and the melting point decreases and there the Ice melts forming water layer. If the pressure is removed the melting point increases and the water layer solidifies. Then the two blocks will stick together into one block. The re-solidification is called relegation.

Ratio of two specific heats

When the temperature of gases change then there is considerable change in volume and pressure. So, gases have two specific heats 1) Specific heat at constant volume 2) Specific heat at constant pressure.

14. Specific heat at constant volume (c_v):- It is the amount of heat required to rise the temperature of unit mass of gas through 1^0C at constant volume.

    S.I. unit is joule/Kg/ K (or) C.G.S unit is cal/gm/^{0}C
15. Specific heat at constant pressure (c_p) :- It is the amount of heat required to rise the temperature of unit mass of gas through 1^0C at constant pressure.

    S.I. unit is joule/Kg/ K (or) C.G.S unit is cal/gm/^{0}C.

From the definition of Bulk modulus $E = \frac{Stress}{Volume\ strain} = -\frac{dP}{dV/_V} = -\frac{VdP}{dV}$

Here the –ve sign indicates that the volume is decreasing with increase of pressure.

Here two elasticities arise

1. Adiabatic elasticity (E_s) - in this entropy is constant.
2. Isothermal elasticity (E_T) - in this temperature is constant.

   Like that of the above equation, we can write,

$$E_S = -V.\left(\frac{\partial P}{\partial V}\right)_S \longrightarrow (1)$$

$$E_T = -V.\left(\frac{\partial P}{\partial V}\right)_T \longrightarrow (2)$$

Dividing the eqn. (1) by eqn. (2)

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T} \text{ (or) } \frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial T}\cdot\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\cdot\frac{\partial S}{\partial V}\right)_T}$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T}\cdot\frac{\left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial S}{\partial V}\right)_T} \longrightarrow (3)$$

The following are the four Maxwell's thermodynamic relations.

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \;\&\; \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Substituting these four relations in eqn. (3)

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

$$\frac{E_S}{E_T} = \left(\frac{\partial S}{\partial T}\right)_P \Big/ \left(\frac{\partial S}{\partial T}\right)_V$$

Multiplying the numerator and denominator by T

$$\frac{E_S}{E_T} = \left(\frac{T\partial S}{\partial T}\right)_P \Big/ \left(\frac{T\partial S}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_P \Big/ \left(\frac{\partial Q}{\partial T}\right)_V \qquad \because T\partial S = \partial Q$$

But $\left(\frac{\partial Q}{\partial T}\right)_P = c_p$ & $\left(\frac{\partial Q}{\partial T}\right)_V = c_v$

$$\boxed{\frac{E_S}{E_T} = \frac{c_p}{c_v}} \text{ (or) } \frac{E_S}{E_T} = \frac{c_p}{c_v} = \gamma \qquad \because \frac{c_p}{c_v} = \gamma$$

The ratio of the specific heat of gas at constant pressure to the specific heat of gas at constant volume is equal to the ratio of the adiabatic elasticity to the isothermal elasticity.

Difference of two specific heats

- In case of specific heat at constant volume (C_V), the total heat supplied is utilized only to increase the internal energy (dU).
- But in case of specific heat at constant pressure (C_P), the heat supplied is utilized to increase the internal energy (dU) and to do some external work (dW).
- So, more heat is required for C_P than for C_V. i.e. $C_P > C_V$.

Here the molar specific heat is taken.

1. Molar specific heat at constant volume (C_V) :- It is the amount of heat required to rise the temperature of one mole of gas through 1^0C at constant volume.

   S.I. unit is joule/mol/ K (or) C.G.S unit is cal/mol/^{0}C

2. Molar specific heat at constant pressure (C_P) :- It is the amount of heat required to rise the temperature of one mole of gas through 1^0C at constant pressure.

S.I. unit is joule/mol/ K (or) C.G.S unit is cal/mol/^{0}C

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

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

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

$$C_P - C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V \qquad \because\ dQ = TdS$$

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

Let the entropy S is a function the thermodynamic independent variables V & T.

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

Dividing this equation by dT

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

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

From Maxwell's 2nd thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

Substituting this value in the above equation

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

Substituting eqn. (2) in eqn.(1)

$$\boxed{C_P - C_V = T\left[\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P\right]} \longrightarrow (3)$$

This is the general equation.

For the ideal or perfect gas

For 1 mole of ideal gas PV = RT

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} \longrightarrow (4)$$

Substituting eqn. (4) in eqn.(3)

$$C_P - C_V = T\left[\frac{R}{V}\cdot\frac{R}{P}\right] = \frac{TR^2}{PV}$$

$$C_P - C_V = \frac{TR^2}{RT} = R \qquad \because\ PV = RT$$

So, for 1 mole of ideal gas $\boxed{C_P - C_V = R}$

Joule-Kelvin effect

Statement:- When a gas is passed through a porous plug from a high constant pressure region to a low constant pressure region, the gas suffers a change in temperature. This effect is called Joule-Kelvin effect or Joule-Thomson effect.

Results :-

- All the gases suffer a change in temperature.
- At room temperature Hydrogen and Helium show heating effect, all other gases show cooling effect.
- The change in temperature is directly proportional to the change in pressure

  i.e. $dT \infty (P_1 - P_2)$ (or) $\frac{dT}{(P_1 - P_2)} = Constant$
- The fall of temperature per unit pressure difference decreases as initial temperature increases. i.e. $\frac{dT}{(P_1 - P_2)}$ *decreases as initial temperature increses.*

In joule-kelvin effect the total enthalpy of the system is constant

This can be written as $\boxed{H = U + PV = Constant}$

On differentiation $dH = dU + P.dV + V.dP = 0$

But $dU = T.dS - P.dV$

Then $dH = (T.dS - P.dV) + P.dV + V.dP = 0$

$$\therefore\ T.dS + V.dP = 0 \longrightarrow (1)$$

Let the entropy S is a function the thermodynamic independent variables P & T.

Then change in S is $dS = \left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \longrightarrow (2)$

Substituting eqn. (2) in eqn. (1)

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

$$[T\left(\frac{\partial S}{\partial P}\right)_T dP + T\left(\frac{\partial S}{\partial T}\right)_P dT] + V.dP = 0 \longrightarrow (3)$$

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

Maxwell's 4th thermodynamic relation is $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ }

Substituting these two values in eqn (3)

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

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

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

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

This is the general equation for joule-kelvin effect

Joule – Kelvin effect for perfect gas

$$\left.\begin{array}{ll}\text{For perfect gas} \quad PV = RT \quad \text{(or)} & V = \frac{RT}{P} \\ \text{Similarly} & \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}\end{array}\right\}$$

Substituting these two equations in the equation of joule-kelvin effect

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[T\frac{R}{P} - \frac{RT}{P}\right] = 0 \quad \text{(or)} \quad \left(\frac{dT}{dP}\right)_H = 0$$

So, the perfect gas has no joule-kelvin effect.

Joule – Kelvin effect for Vander – Waal's gas

The Vander-Waal's equation of a gas is $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

Differentiating this equation with respect to V at constant pressure

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

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

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

Multiplying the numerator and denominator by $(V - b)$

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

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

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R\,(V-b)}{\left[RT - (V^2 + b^2 - 2Vb)\left(\frac{2a}{V^3}\right)\right]} = \frac{R\,(V-b)}{\left[RT - \left(\frac{2a}{V} + \frac{2ab^2}{V^3} - \frac{4Vab}{V^2}\right)\right]}$$

a & b values are small and their product ab is negligible. The terms containing ab are neglected.

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

Multiplying both sides by T $\quad T\left(\frac{\partial V}{\partial T}\right)_P = \frac{RT\,(V-b)}{\left[RT - \frac{2a}{V}\right]}$

Substituting this equation in the equation of joule-kelvin effect

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[\frac{RT\,(V-b)}{\left[RT - \frac{2a}{V}\right]} - V\right]$$

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[\frac{\frac{RT\,(V-b)}{RT}}{\frac{\left[RT - \frac{2a}{V}\right]}{RT}} - V\right]$$

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[\frac{(V-b)}{\left[1 - \frac{2a}{VRT}\right]} - V\right]$$

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[(V - b)\left[1 - \frac{2a}{VRT}\right]^{-1} - V\right]$$

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[(V - b)\left[1 + \frac{2a}{VRT}\right] - V\right]$$

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[\left(V - b + \frac{2a}{RT} - \frac{2ab}{VRT}\right) - V\right]$$

$$\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left[\left(V - b + \frac{2a}{RT} -\right) - V\right] \qquad \because ab\ is\ negligible,\ \frac{2ab}{VRT}\ is\ neglected$$

$$\boxed{\left(\frac{dT}{dP}\right)_H = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)}$$

This is joule-kelvin effect equation for the Vander – Waal's gas.

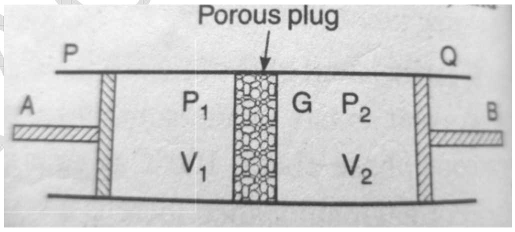
Chapter - IV

Low temperature Physics

Different methods to attain low temperatures

1. -22^0C temperature can be obtained by adding salt to ice.
2. Boiling a liquid at low pressure :- In this method the liquid takes the latent heat of vaporization from the liquid it self. So, its temperature decreases. Here the boiling point decreases with the decrease of pressure. Low temperatures can be obtained by this method also.
3. Joule-Kelvin effect :- This method is used to decrease the temperature of gases.
4. Adiabatic demagnetization :- In this method magnetized material is demagnetized in adiabatic process. Using this method nearly 0.0014 K temperature can be obtained.
5. Refrigeration :- This is also one type of adiabatic expansion. This process can also be used to decrease the temperature.

Joule-Kelvin effect (Porous plug experiment)



- Joule-Kelvin experiment is as shown in figure.
- PQ is the thermally insulated hallow cylinder. The porous plug G,(Wool or cotton having porous) divides the cylinder in to two parts.
- A and B are two non-conducting pistons on both sides.
- The gas in left compartment is at higher constant pressure P_1 and in right compartment the gas has lower constant pressure P_2.
- When the gas in left compartment at higher pressure P_1 is compressed, then the gas passed through the porous plug and goes in to right compartment of lower constant pressure P_2. Then the distance between the molecules increase and the gas suffers change in temperature.

Statement:- When a gas is passed through a porous plug from a high constant pressure region to a low constant pressure region, the gas suffers a change in temperature. This effect is called Joule-Kelvin effect or Joule-Thomson effect.

Results :-

- All the gases suffer a change in temperature.
- At room temperature Hydrogen and Helium show heating effect, all other gases show cooling effect.
- The change in temperature is directly proportional to the change in pressure

  i.e. $dT \infty (P_1 - P_2)$ (or) $\frac{dT}{(P_1 - P_2)} = Constant$
- The fall of temperature per unit pressure difference decreases as initial temperature increases. i.e. $\frac{dT}{(P_1 - P_2)}$ *decreases as initial temperature increses.*

Temperature of inversion :- The temperature at which the gas shows no Joule-Kelvin effect is called the inversion temperature of that gas.

- The temperature of inversion is different for different gases.

Explanation :- Let P_1, V_1, T_1 and P_2, V_2, T_2 be the pressures, volumes and temperatures of the gas on left and right compartments respectively ($P_1 > P_2$). Let unit mass of gas passed through the porous plug & U_1, U_2 be the internal energies before and after passing through the porous plug.

Work done on the gas by the piston A = P_1V_1
Work done by the gas on the piston B = P_2V_2
Net work done by the gas = $(P_2V_2 - P_1V_1)$
The system is thermally isolated, so, the work is done by utilizing its internal energy.
i.e. Work done = Decrease in internal energy

$$(P_2V_2 - P_1V_1) = (U_1 - U_2)$$

$$P_2V_2 + U_2 = P_1V_1 + U_1 \quad \text{(or)} \quad PV + U = \text{Constant}$$

This is enthalpy. So, Joule-Kelvin effect follows the law of conservation of enthalpy.

Applications

Perfect gas :- Perfect gas obeys Boyle's law at all temperatures and pressures.
So, $P_1V_1 = P_2V_2$ then, $U_1 = U_2$ i.e. Internal energy is constant.
Internal energy = Potential energy (ρ)+ Kinetic energy(k)
Potential energy is zero ($\rho = 0$) because there is no intermolecular attraction in perfect gas. So, kinetic energy alone is constant i.e. $k_1 = k_2$ (or) $T_1 = T_2$. No heating or cooling effect.

Real gas :-

Case 1:- At Boyle's temperature :- For real gas at Boyle's temperature

$P_1V_1 = P_2V_2$ then, $U_1 = U_2$ i.e. Internal energy is constant.

So, at this temperature no heating effect or no cooling effect.

Case 2:- Below Boyle's temperature :- Below Boyle's temperature the PV value decreases as P increases. So, $P_2V_2 > P_1V_1$ i.e. $U_1 > U_2$ $\because$ $P_2V_2 + U_2 = P_1V_1 + U_1$

After passing through the porous plug the internal energy decreases. i.e. Cooling effect takes place.

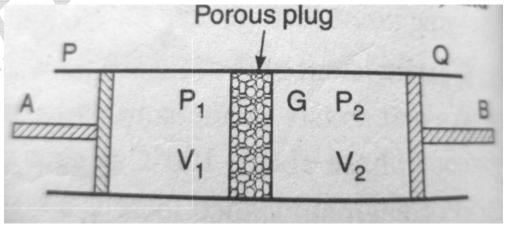
Case 3:- Above Boyle's temperature :- Above Boyle's temperature the PV value increases as P increases. So, $P_1V_1 > P_2V_2$ i.e. $U_2 > U_1$ $\because$ $P_2V_2 + U_2 = P_1V_1 + U_1$

After passing through the porous plug the internal energy increases. i.e. Heating effect takes place.

Distinction among Joule's expansion, adiabatic expansion and Joule-Kelvin expansion

S.No.	Joule's expansion	Adiabatic expansion	Joule-Kelvin expansion
1.	This is free expansion & the gas expands in to vacuum.	The compressed gas suddenly expands in to air.	Here gas flows from high pressure to low pressure.
2.	This is slow process.	This is quick process.	This is slow process.
3.	No surrounding medium.	Surrounding medium is air.	It has surrounding medium.
4.	No external work is done.	External work is done against atmosphere.	External work is done on the gas and by the gas.
5.	Internal work is done against intermolecular attraction.	Internal work is done against intermolecular attraction.	Internal work is done against intermolecular attraction.
6.	Heating or cooling effect takes place depending upon the initial temperature.	The gas gets cooled as it do external work.	Heating or cooling effect takes place depending upon the initial temperature.

Expression for Joule-Thomson cooling



- ❖ Joule-Kelvin experiment is as shown in figure.
- ❖ PQ is the thermally insulated cylinder. The porous plug G, (Wool or cotton having porous) divides the cylinder in to two parts.
- ❖ A and B are two non-conducting pistons on both sides.
- ❖ The gas in left compartment is at higher constant pressure P_1 and in right compartment the gas has lower constant pressure P_2.
- ❖ When the gas in left compartment at higher pressure P_1 is compressed, then the gas passed through the porous plug and goes in to right compartment of lower constant pressure P_2.
- ❖ Let the V_1 and V_2 be the volumes of one gm-mole of gas, before and after passing through the porous plug.

External work done on the gas by the piston A = P_1V_1
External work done by the gas on the piston B = P_2V_2
Net external work done by the gas $W_1 = (P_2V_2 - P_1V_1)$

In addition to this external work, some internal work (W_2) is also done. This work is done to pull the molecules apart against the intermolecular attraction. Vander Waal's equation for internal work (W_2)

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

The total work done $W = W_1 + W_2$

$$W = W_1 + W_2 = (P_2V_2 - P_1V_1) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) \longrightarrow \quad (1)$$

According to Vander Waal's equation $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

$$\left(PV + \frac{a}{V} - Pb - \frac{ab}{V^2}\right) = RT$$

The values of a, b are very small, so, $\frac{ab}{V^2}$ value can be neglected.

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

similarly $\quad P_1V_1 = RT - \frac{a}{V_1} + P_1b$

$$P_2V_2 = RT - \frac{a}{V_2} + P_2b$$

From the above two equations $P_1V_2 - P_1V_1 = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - b(P_1 - P_2) \longrightarrow$ (2)

Substituting eqn. (2) in (1) $W = a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - b(P_1 - P_2) + a\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$

$$\therefore W = 2a\left(\frac{1}{V_1} - \frac{1}{V_2}\right) - b(P_1 - P_2) \longrightarrow (3)$$

As $\frac{1}{V_1}, \frac{1}{V_2}$ are small, to get these values we use the approximation PV = RT

(Or) $\frac{1}{V} = \frac{P}{RT}$ Then $\frac{1}{V_1} = \frac{P_1}{RT}$ & $\frac{1}{V_2} = \frac{P_2}{RT}$

Then eqn. (3) becomes $W = 2a\left(\frac{P_1}{RT} - \frac{P_2}{RT}\right) - b(P_1 - P_2) = \frac{2a}{RT}(P_1 - P_1) - b(P_1 - P_2)$

$$W = (P_1 - P_1)\left(\frac{2a}{RT} - \mathrm{b}\right)$$

This system is thermally insulated.

So Work done by the system = Decrease in the internal energy of the system

The decrease in internal energy for 1 gm-mole of gas = - C_P.dT

C_P = Molar specific heat at constant pressure, dT = Fall of temperature.

$$-C_P.\mathrm{dT} = (P_1 - P_1)\left(\frac{2a}{RT} - \mathrm{b}\right)$$

$\boxed{\mathrm{dT} = -\frac{(P_1 - P_1)}{C_P}\left(\frac{2a}{RT} - \mathrm{b}\right)}$ All the units in S.I. System.

Case 1:- If $\left(\frac{2a}{RT} - \mathrm{b}\right)$ is positive i.e. $\frac{2a}{RT} > b$ (or) $\frac{2a}{R\mathrm{b}} > T$ then dT = -ve and the gas is cooled.

Case 2:- If $\left(\frac{2a}{RT} - \mathrm{b}\right)$ is negative i.e. $\frac{2a}{RT} < b$ (or) $\frac{2a}{R\mathrm{b}} < T$ then dT = +ve and the gas is heated.

Case 3:- If $\left(\frac{2a}{RT} - \mathrm{b}\right) = 0$ i.e. $\frac{2a}{RT} = \mathrm{b}$ (or) $\frac{2a}{R\mathrm{b}} = T$ then dT = 0 and the temperature is unchanged.

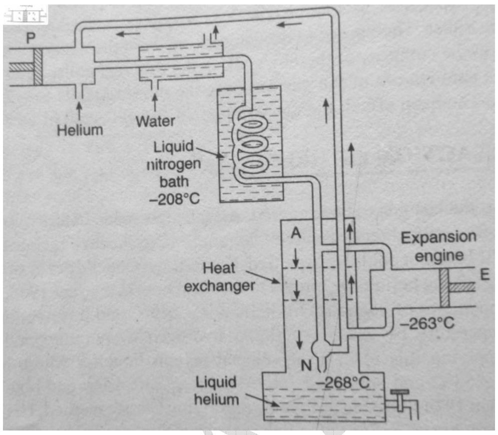
This temperature is called temperature of inversion (T_i). $\boxed{T_i = \frac{2a}{R\mathrm{b}}}$

Boyle's temperature (T_B) :- The temperature at which the gas obeys Boyle's law is called the Boyle's temperature of that gas.

Inversion temperature (T_i) :- The temperature at which the gas shows no Joule-Kelvin effect is called the inversion temperature of that gas.

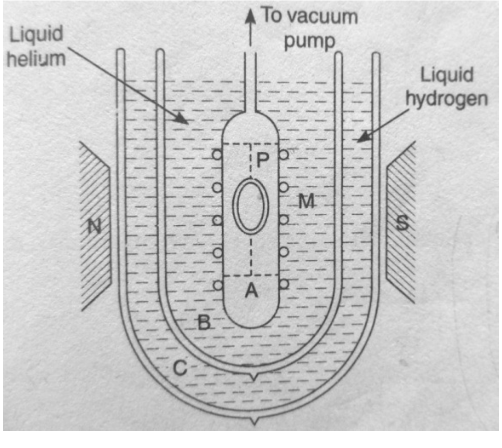
Critical temperature (T_c) :- The minimum temperature above which the gas can not be liquefied is called the critical temperature of that gas.

Helium liquefier – Kapitza's method



- Helium is the gas liquefied lastly because its critical temperature is 5K, Boyle's temperature is 17K and inversion temperature is 34K. All these values are low. So it is highly difficult to liquefy Helium.
- In this method no lubricant is used and no hydrogen liquid is used. The apparatus is as shown in figure.
- Pure and dry helium gas is compressed to 30 atmospheres by compressor P.
- The heat generated due to compression is removed by passing the tube containing helium gas through a cold water jacket.
- The gas is pre-cooled to -208°C by passing it through liquid nitrogen bath. Here the liquid nitrogen boils at reduced pressure.
- This pre-cooled gas is divided in to two parts in the heat exchanger A. one part is passed through the expansion engine E. Here the gas cooled to -263°C due to adiabatic expansion.
- This cooled gas raises up in the heat exchanger and cools the second part which is coming towards the nozzle N.
- This second part expands at the nozzle N and it is liquefied at -268 °C.
- The liquefied helium is collected in the Dewar flask and the non-liquefied part goes back to the compressor through the heat exchanger. The same process is repeated to get more liquid.

Adiabatic demagnetization



- ❖ If a paramagnetic material is magnetized (molecular magnets are set in the direction of applied magnetic field) then work is done on the material. So, its internal energy and its temperature increases.
- ❖ Principle :- When a para magnetic already magnetized is suddenly demagnetized adiabatically its temperature falls slightly. This is called adiabatic demagnetization.

Construction :-

- ❖ A paramagnetic substance (specimen), gadolinium, is suspended in a vessel A. The vessel A is connected to a vacuum pump. A coil M is wound on the vessel A & the coil is used to measure temperature by susceptibility measurement method.
- ❖ The vessel A is placed in a Dewar flask B containing liquid helium at 1 K temperature.

- The flask B is placed in another Dewar flask C containing liquid hydrogen.
- This total arrangement is placed between the two poles of a strong magnet (N-S).

Working :-

- First the vessel A is filled with helium gas at low temperature because at low temperature helium is highly conductive. So, the paramagnetic material comes in to thermal contact with the liquid helium at 1 K & cooled to 1K.
- Now the magnetic field is switched on and the paramagnetic substance magnetized & is heated. This heat flows out through helium gas in to liquid helium. The temperature of substance falls to 1 K.
- After this, the helium gas is pumped out and the paramagnetic substance is thermally isolated.
- Now the magnetic field is switched off and the temperature of paramagnetic substance falls due to adiabatic demagnetization.
- The fall in temperature of the substance is measured by susceptibility measurement method using the coil wound on vessel A.
- The lowest temperature so far attained is 0.0014 K.

Theory (or) Expression for fall of temperature

Let the magnetic induction of field in which paramagnetic substance is placed = B

Intensity of magnetization per gm.mole. of substance = I

Change in intensity of magnetization per gm.mole. of substance = dI

Work done by magnetic field on paramagnetic substance during magnetization = B.dI

Work done by paramagnetic substance during demagnetization dW = - B.dI

From 1st law of thermodynamics $dQ = dU + dW$ (or) $dQ = dU - B.dI$

But $dQ = T.dS$ So, $T.dS = dU - B.\,dI \longrightarrow (1)$

As per 3rd Maxwell's thermodynamic relation between entropy and pressure is

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

To get a similar relation to eqn. (1) it is to substitute –B for P and I for V

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

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

If m is the mass of the specimen and C_B is the specific heat at constant field, then

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

Substituting eqn. (3) in (2) $\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{mC_B}\left(\frac{\partial I}{\partial T}\right)_B$

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

But susceptibility of the specimen $\chi = \frac{Intensity\ of\ magnetization\ of\ specimen}{Magnetic\ induction\ of\ the\ field} = \frac{I}{B} \longrightarrow (5)$

& Susceptibility is inversely proportional to absolute temperature.

$$\chi \infty \frac{1}{T} \quad (or) \qquad \chi = \frac{C}{T} \longrightarrow \quad (6)$$

Here C is proportionality constant.

Comparing the eqns. (5) & (6) $\frac{I}{B} = \frac{C}{T}$ (or) $I = \frac{CB}{T} \longrightarrow$ (7)

Substituting eqn. (7) in eqn. (4) $\partial T = -\frac{T}{mC_B}\left[\frac{\partial}{\partial T}\left(\frac{CB}{T}\right)\right]\partial B$

$$\partial T = -\frac{T}{mC_B}\left[-\left(\frac{CB}{T^2}\right)\right]\partial B \quad \text{(or)} \quad \partial T = \frac{C}{mC_BT}.B.\partial B$$

Integrating this eqn. $\int_{T_i}^{T_f} \partial T = \frac{C}{mC_BT}\int_{B_i}^{B_f} B.\partial B$

$$T_f - T_i = \frac{C}{mC_BT}\frac{{B_f}^2 - {B_i}^2}{2}$$

Here T_i & T_f are initial and final temperatures and B_i & B_f are initial and final magnetic inductions.

On demagnetization the final magnetic induction is zero. $B_f = 0$

Also $\frac{C}{m} = k$ is called Curie's constant per unit mass.

Substituting these values in the above equation.

$$\boxed{T_f - T_i = -\frac{k}{2C_BT}\,{B_i}^2}$$

The –ve sign indicates that the temperature is falling.

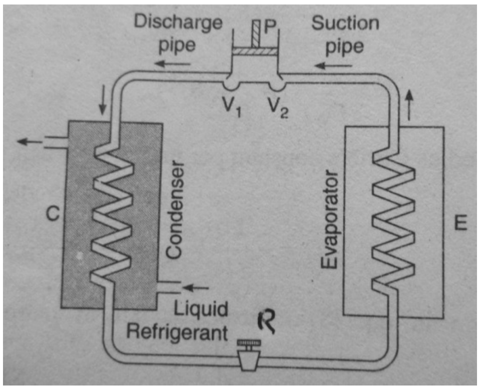
Refrigerator

A machine used for producing low temperature below surroundings and maintaining the enclosure at that temperature is called refrigerator.

Refrigerating machines are of two types 1. Vapour compression machine. 2. Vapour absorption machine.

Vapour compression machine (or) Frigidaire

- Refrigerator maintains an adiabatic enclosure at low temperature.
- The principle involved in producing low temperature is, evaporating the liquid under reduced pressure.
- Circulates the evaporating liquid around the enclosure. The liquid which on evaporation produces cooling is called refrigerant.



Construction and working

- The Frigidaire consists of a compression pump P in which the refrigerant is compressed. There are two valves V_1, V_2 below this pump.
- If the piston moves up valve V_1 closes and the valve V_2 opens & sucks the low pressure vapour from the evaporator E.

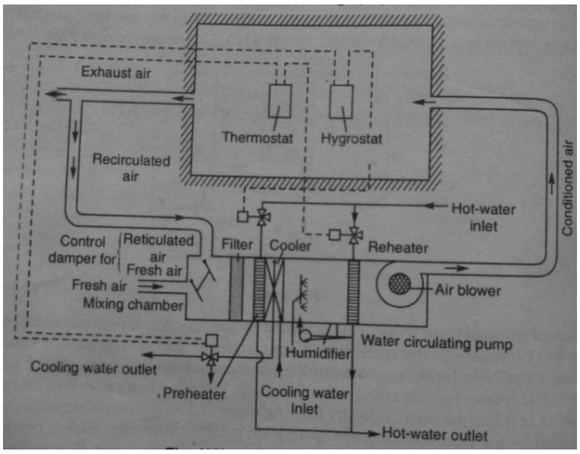
- If the piston is pushed down valve V_1 opens & valve V_2 is closed. Now the vapour under high pressure enters in to the condenser coil C. The condenser coil is enclosed in a cold water bath. Under high pressure and low temperature the vapour refrigerant is liquefied in the coil.
- The liquid refrigerant is now passed through the regulator R in to evaporator E. Due to low pressure, the liquid evaporates in the evaporator.
- For evaporation refrigerant takes heat from it self. So, it cools.
- Also when the liquid evaporates in the evaporator it takes latent heat of vaporization from the cold storage space.
- This process is repeated again and again. The temperature of the cold storage space falls.

Properties of an ideal refrigerant (Not important)

1. The refrigerant should have low boiling point and low freezing point.
2. It should be vapour at normal temperature and pressure
3. It should be non flammable & non explosive.
4. It should not have bad effects on the stored food material.
5. It should have high thermal conductivity.
6. The latent heat of vaporization of the refrigerant liquid must be large.
7. The specific volume should be small in order to reduce the size of compressor.
8. The pressure necessary to liquefy the vapour in condenser coil must be small.

Air conditioning machine

- The function of the air conditioning machine is to keep the temperature and humidity of the air in a room to required comfortable levels.
- Human body is comfortable at 20 ^{o}C to 25 ^{o}C temperature and 35% to 75% relative humidity.



A.C. machine has the following parts

1) Thermostat to control the temperature
2) Hygrostat to control the humidity
3) Control damper to circulate air and fresh air
4) Filter to absorb the dust in the air
5) Cooling and heating systems
6) Air blower or fan

* A part of the air from air conditioned room is re-circulated. The re-circulated air is mixed with the fresh air in mixing chamber.

* There are filters in the mixing chamber which absorb dust from the mixed air. The cleaned air is preheated by means of hot water through pipes in the mixing chamber. This is done because, warm air can absorb more water vapour.

* Also in the mixing chamber, a part of air is cooled by the cooler system. The moisture content and temperature of the air emerging out from the cooler are adjusted to the desired values.

* The air coming out from the cooler is mixed with the air coming straight from the Pre-heater. Therefore, a mixture of desired temperature and humidity is obtained.

* If the humidity is very low then water is added to air mixture by means of spray nozzles. By doing so the temperature is also increased.

* To maintain the desired temperature, the air again passed through a reheater. As a result we get the air of desired temperature and humidity.

* The air blower or fan behind the reheater forces the conditioned air through ducts into the room.

Applications &Properties of substances at low temperatures

1) At low temperatures below 90 K most of the chemical reactions ceases. At these temperatures animals and vegetable matter can be preserved without purification.
2) Materials like cotton and wool exhibit the property of fluorescence when exposed to the temperature of liquid air.
3) At a temperatures below 83K lead loses elasticity exhibits plastic nature.
4) The substances like rubber and glass become extremely brittle get these temperatures. Rubber cooled to such a low temperatures breaks into pieces when hammered.
5) For all substances the atomic heat (product of atomic weight and specific heat) becomes zero at the absolute zero.
6) Oxygen is not paramagnetic substance in the gaseous state but when they are converted into liquid at low temperature it becomes paramagnetic substance.
7) At low temperatures for paramagnetic salts like Copper Sulphate $\chi \infty \frac{1}{T}$
8) The entropy of a substance becomes zero when it is exposed to very low temperature.
9) The electrical resistance of most metals decrease as the temperature is reduced. At a particular temperature the resistance becomes zero i.e. the conductivity becomes infinity and this property is called superconductivity.
10) Below 2.17 K helium is called as Helium II and it exhibits super fluidity. Its viscosity becomes very low and it can pass through a capillary tube without any resistance, this property is known as super fluidity.

Effects of chlorofluorocarbons on ozone layer

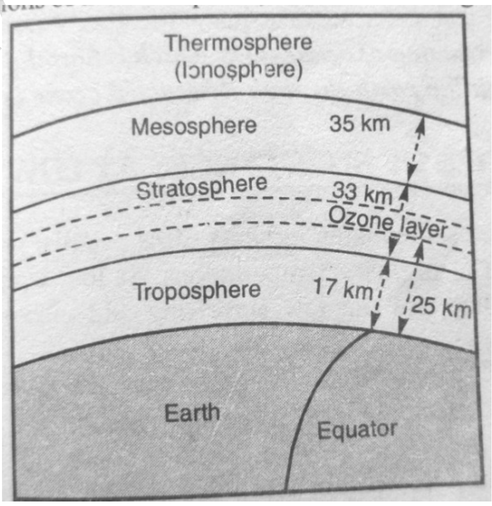
1) The chloro-fluoro carbons are responsible for the destruction of ozone layer.
2) Already about 5% of ozone layer has been depleted at global level.
3) The depletion of ozone layer is greatest over the south pole where about 50% hole is formed in the ozone layer.
4) The hole in the ozone layer results in increase ultraviolet radiations directly reaching the earth.
5) These radiations produce harmful effects on human life, plant life and underwater aquatic life.

Harmful effects of ultraviolet radiation

1) It damages the DNA of reproductive molecules in all living beings.
2) It increases the skin cancer.
3) It increases the damage of human and plant life.
4) It reduces the rate and efficiency of photosynthesis.
5) It effects the global climate and increases the global warming.

Significance of Ozone layer

1) The gaseous layer surrounding the earth about 500 Km thickness is called atmosphere.
2) The atmosphere consists of N_2, O_2, CO_2, H_2, O_3 etc. The atmosphere is divided into four regions 1. Troposphere 2. Stratosphere 3. Mesosphere and 4. Thermosphere.
3) The atmospheric layer above 25 Km from the surface of the earth is called ozonosphere or ozone layer.
4) Ozone molecules present in this layer, these molecules absorb ultraviolet radiation coming from the Sun to the atmosphere.



5) The ozone decomposes into O_2 and mono oxygen (O) by absorbing ultraviolet radiation.
6) The ozone layer protects us from direct exposure of ultraviolet radiation.

Chapter - V

QUANTUM THEORY OF RADIATION

Properties of thermal radiation

1. The radiation travels in vacuum.
2. It travels in straight line path.
3. It undergoes reflection, refraction and total internal reflection.
4. It follows inverse square law.
5. It exhibits the phenomenon of interference, diffraction and polarization.
6. When the radiation falls on a surface it exerts some pressure on the surface, called thermal pressure.

Some definitions

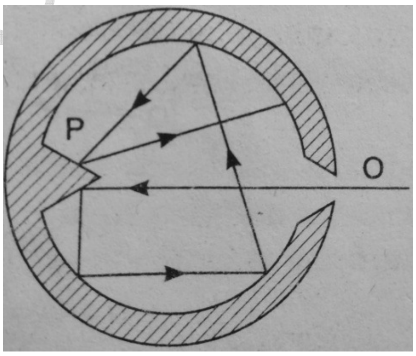
1) Total energy(U) :- The total amount of energy contained with in the system due to all the wave lengths is called total energy. The unit is joule.
2) Spectral energy (U_λ):- The spectral energy for a particular wavelength is the energy contained with in the system of particular wave length in unit wave length range.
   The unit is joule.
3) Total energy density(u) :- The energy per unit volume due to all the wave lengths is called total energy density. The unit is joule/m^3.
4) Spectral energy density (u_λ):- The spectral energy density for a particular wavelength is the energy per unit volume of particular wave length in unit wave length range.
   The unit is joule/m^3.
5) Total emissive power (e) :- The total emissive power of a surface at a particular temperature is the energy emitted from unit area in unit time due to all the wave lengths.
   The unit is joule/sec/ m^2 (or) watt/m^2.
6) Total absorptive power (a) :- The total absorptive power of a surface at a particular temperature is the ratio of the energy absorbed by the surface to the energy incident on the surface on the same area in same time. It has no units.
7) Spectral emissive power (e_λ) :- The spectral emissive power of a surface at a particular temperature for a particular wave length is the energy emitted by the surface from unit area in unit time, of particular wave length in unit wave length range.
   The unit is joule/sec/ m^2 (or) watt/m^2.
8) Spectral absorptive power (a_λ) :- The spectral absorptive power of a surface at a particular temperature is the ratio of the energy absorbed by the surface of particular wave length in unit wave length range to the energy incident on the surface of particular wave length in unit wave length range on the same area in same time. It has no units.

Black body

Definition :- A body that absorbs all the radiation that incident on it is called the black body.

- So, its absorptive power is one ($a_\lambda = 1$).
- As per Kirchhoff's law good absorbers are good emitters. So, black body is good absorber as well as good emitter.
- When this is heated to a particular temperature, it emits the radiation of all wave lengths & gives continuous spectrum.
- The wave length of emitted radiation depends on the temperature of the black body but not on the nature of material of the body.
- There is no perfectly black body in the universe. But Platinum black and lamp black are considered as black bodies because their absorptive power is nearly 0.98.

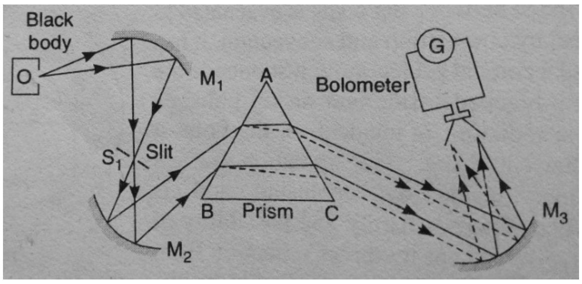
Fery's black body



- Fery's black body is a double walled spherical body.
- The space between the two walls is evacuated to avoid loss of heat by conduction and convection.
- The outer surface of outer sphere is polished with Nickel and the inner surface of the inner sphere is coated with lamp black.
- It has a small opening O, for the entrance of radiation into the black body. A conical projection P, is arranged quite opposite to the opening to avoid normal incidence of radiation.
- The radiation entered through the opening will get multiple reflections on the black surface. At each reflection some energy is absorbed. Like this, the total energy is absorbed.
- So, the opening acts as the black body.

Energy distribution of black body radiation

Lummer & Pringsheim experiment

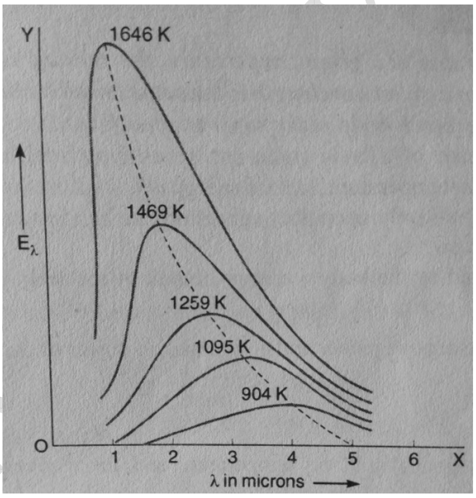


- The divergent beam of radiation from the black body is made convergent beam by the concave mirror M_1 and this beam is made parallel by the concave mirror M_2.
- This parallel beam of radiation incident on Fluorspar prism. This beam is dispersed in to different wave lengths.
- Different wave lengths come out in different directions.

- ✓ Rays of same wave length are parallel to one another.
- ✓ The concave mirror M_3 focuses different wave lengths in different directions.
- ✓ A bolometer is placed in the path of radiation. By rotating the mirror M_3, different wave lengths can be focused on bolometer.
- ✓ The bolometer directly measures the incident radiation (E_λ).
- ✓ E_λ is measured for different values of λ. The experiment is repeated by keeping the black body at different temperatures.

Properties

The graph drawn by taking E_λ on Y-axis and λ on X-axis is called characteristic curve.



1. The black body emits all wave lengths. So, it gives continuous spectrum.
2. The energy is distributed non-uniformly i.e. the energy emitted is small at very shorter wave lengths and at very longer wave lengths.
3. The curve is asymmetric about the peak.
4. The area below the curve is numerically equal to the total radiation emitted by the body.
5. The E_λ value increases as the temperature of the body increases.
6. The peak or the most probable wave length (λ_m) decreases as temperature (T) increases. i.e. Wein's displacement law $\lambda_m.T$ = Constant.

Laws of thermal radiation

1. Kirchoff's law :- At a given temperature and for a given wave length, the ratio of emissive power to the absorptive power is same for all the bodies and it is also equal to emissive power of the black body at that temperature.

   $$\boxed{\frac{e_\lambda}{a_\lambda} = E_\lambda}$$

2. Stefan – Boltzmann law :- The amount of radiant energy emitted by a black body per unit area per unit time is directly proportional to the fourth power of its absolute temperature.

   $$E \propto T^4 \quad (or) \quad \boxed{E = \sigma T^4}$$

   Here σ is called Stefan's constant. Its value is 5.67 x 10^{-8} watt/m^2/K^4.

   If T_B is the temperature of the body and T_S is the temperature of the surroundings.

   Then the net amount of energy emitted $\boxed{E = \sigma\,(T_B^4 - T_S^4)}$

   Here $\sigma\,T_B^4$ is the energy emitted by the body and $\sigma\,T_S^4$ is the energy taken by the body from the surroundings.

3. Wein's displacement law :- The product of the wave length corresponding to maximum energy emitted by the black body and its absolute temperature is constant.

   $$\boxed{\lambda_m.T = constant}$$

Here λ_m = wave length corresponding maximum energy emitted.

T = Absolute temperature of the black body.

4. Wein's law (or) Wein's formula :-

The energy distribution emitted by the black body $\boxed{E_\lambda d\lambda = A.\lambda^{-5}.e^{-B/\lambda T} d\lambda}$

Here A & B are constants λ = wave length T = absolute temperature.

5. Rayleigh – Jean's law :-

The energy distribution emitted by the black body $\boxed{E_\lambda d\lambda = \frac{8\pi KT}{\lambda^4} d\lambda}$

Here K= Boltzmann constant λ = wave length T = absolute temperature.

6. Planck's law :-

The energy distribution emitted by the black body $\boxed{E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)} d\lambda}$

Here h = Planck's constant K= Boltzmann constant λ = wave length T = absolute temperature.

Wein's displacement law

Statement :- The product of the wave length corresponding to maximum energy emitted by the black body and its absolute temperature is constant.

$$\lambda_m . T = constant$$

Derivation :- Consider the black body in spherical shape having volume V and having perfectly reflecting walls. The body is at a temperature T. It is having energy density u.

The total internal energy U = uV $\longrightarrow$ (1)

When the radiation reflects from the wall, the body expands and the volume increases by dV. This is adiabatic expansion. i.e. dQ = 0

According to the 1st law of thermodynamics dQ = dU + P.dV = 0 $\longrightarrow$ (2)

But thermal pressure $P = \frac{1}{3}u \longrightarrow$ (3)

Substituting eqns. (1) and (3) in (2)

$$d(uV) + \frac{1}{3}u\,dV = 0$$

$$u\,dV + V\,du + \frac{1}{3}u\,dV = 0$$

Or

$$\frac{4}{3}u\,dV + V\,du = 0$$

Dividing this equation by uV

Then

$$\frac{4}{3}\frac{dV}{V} + \frac{du}{u} = 0$$

Integrating this equation

$$\int \frac{4}{3}\frac{dV}{V} + \int \frac{du}{u} = \text{constant}$$

$$\frac{4}{3}\log_e V + \log_e u = \text{constant}$$

$$\log_e V^{\frac{4}{3}} + \log_e u = \text{constant}$$

$$V^{\frac{4}{3}}.u = constant$$

$$\text{But} \quad u = \sigma T^4$$

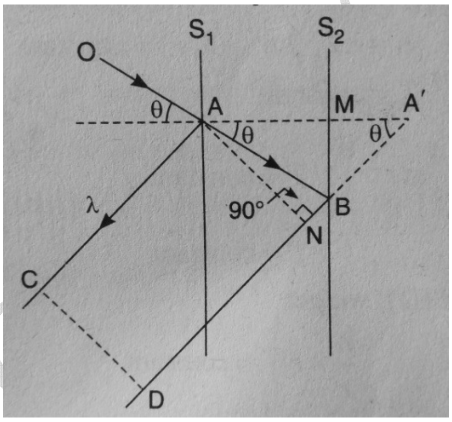
$$\therefore \quad V^{\frac{4}{3}} . \sigma T^4 = constant$$

Taking the 4th power root to the above equation $V^{\frac{1}{3}} . T = constant$

Here V is the volume of the spherical black body. So, $V = \frac{4}{3}\pi r^3$ r = radius of black body

$$\left(\frac{4}{3}\pi r^3\right)^{\frac{1}{3}} . T = constant \quad \text{(or)} \quad \boxed{r.T = constant} \longrightarrow (4)$$

Change in wave length per reflection



- ✪ As the radiation reflects from the wall of the black body, the wall moves away due to thermal pressure.
- ✪ Let the S_1 and S_2 be the two positions of the surface of the black body when the crests of the 1st and 2nd waves reflect. The distance between them $AM = vT$
  v = Velocity of the moving surface and T= Time period of the wave reflected.
- ✪ The paths of 1st wave and 2nd wave are OAC and OBD.
- ✪ The path difference between them = change in wave length per reflection.
- ✪ Draw two perpendicular lines AN and CD from A & C on to BD. Also extend BD upto A^1.

Change in wave length per reflection $d\lambda^1 = (AB + BD) - AC$

$$d\lambda^1 = (AB + BN + ND) - AC$$

But $ND = AC$ So, $d\lambda^1 = (AB + BN)$

But $AB = A^1B$ So, $d\lambda^1 = (A^1B + BN) = A^1N$

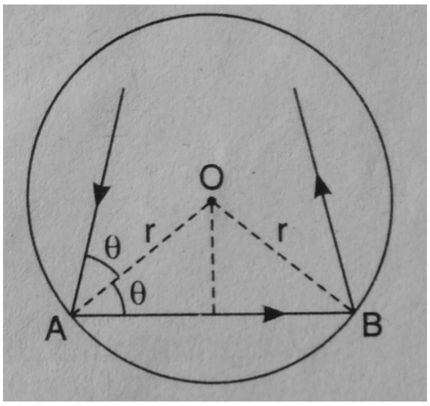
From the right angled triangle $A A^1 N$ $\cos\theta = \frac{A'N}{AA'}$ $\therefore A'N = AA' \cos\theta$

But $AM = MA^1 = vT$ So, $AA^1 = 2vT$

$$\therefore d\lambda' = A'N = 2vT\cos\theta$$

$$\boxed{d\lambda' = 2v\frac{\lambda}{c}\cos\theta} \longrightarrow (5) \qquad \because T = \frac{\lambda}{c}$$

No. of reflections



From the figure, the ray has to travel (2r cosθ) distance for each reflection.

No. of reflections per second

$$= \frac{Distance}{Distance\ travelled\ per\ reflection} = \frac{c}{2\,r\,cos\theta}$$

No. of reflections in dt time $\boxed{n = \frac{c.dt}{2\,r\,cos\theta}} \longrightarrow (6)$

Change in wave length in dt time

$$d\lambda = d\lambda'.n = 2v\frac{\lambda}{c}\cos\theta . \frac{c.dt}{2\,r\,cos\theta}$$

$$d\lambda = \lambda . \frac{v.dt}{r}$$

and $v.dt = dr$ = Increase in the radius of the black body

$$\frac{d\lambda}{\lambda} = \frac{dr}{r}$$

Integrating this equation $\int \frac{d\lambda}{\lambda} = \int \frac{dr}{r}$ (or) $\log_e \lambda = \log_e r + \log_e C$

$$\log_e \frac{\lambda}{r} = \log_e C \quad \text{(or)} \quad \frac{\lambda}{r} = C \quad \text{(or)} \quad \boxed{r = \frac{\lambda}{C}} \longrightarrow (7)$$

Substituting eqn. (7) in eqn. (4)

$$\frac{\lambda}{C}.T = constant \quad \text{(or)} \quad \lambda.T = constant$$

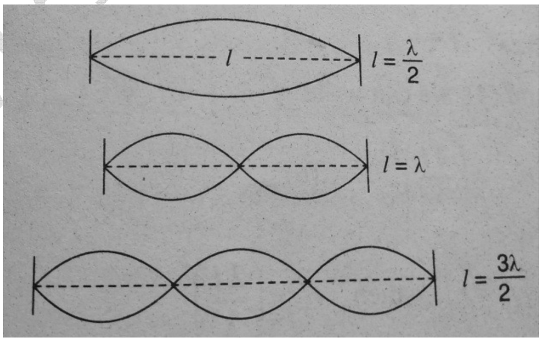
For most probable wave length λ_m $\boxed{\lambda_m.T = constant}$

Rayleigh-Jeans formula

- Rayleigh-Jeans formula, for the energy distribution of black body radiation, is based on electromagnetic theory and statistical mechanics.
- A black particle is placed in a cubical enclosure having perfectly reflecting walls & side length l.
- As per electromagnetic theory, the particle emits the waves of different wave lengths.
- These waves reflect from different walls of the enclosure and form stationary waves.

Ex:- If a wire of length l, vibrates in n loops

$l = n\frac{\lambda}{2}$ where n = 1, 2, 3, ……. ∞



- ✓ Similar is the case with the enclosure of side l, filled with radiation. Every allowed frequency is called a mode of vibration.
- ✓ Let n_x, n_y and n_z be the no. of loops along the 3 edges of the cube respectively.
- ✓ If these waves are making α, β, γ angles with the axes.

Then

$$l\,Cos\alpha = n_x\frac{\lambda}{2}$$
$$l\,Cos\beta = n_y\frac{\lambda}{2}$$
$$l\,Cos\gamma = n_z\frac{\lambda}{2}$$

Squaring and adding these equations

$$l^2\,(Cos^2\alpha + Cos^2\beta + Cos^2\gamma) = \left(\frac{\lambda}{2}\right)^2 (n_x^2 + n_y^2 + n_z^2)$$

But $(Cos^2\alpha + Cos^2\beta + Cos^2\gamma) = 1$

$$l^2 = \left(\frac{\lambda}{2}\right)^2 (n_x^2 + n_y^2 + n_z^2) \quad \text{(or)} \quad (n_x^2 + n_y^2 + n_z^2) = \left(\frac{2l}{\lambda}\right)^2$$

This equation represents a sphere of axes n_x, n_y & n_z and radius $r = \frac{2l}{\lambda}$

Here each set of $(n_x, n_y$ & $n_z)$ will give one mode of vibration.

So, the total no. of modes of vibration = the total no. of possible sets of $(n_x, n_y \,\&\, n_z)$

For more clarity, take an example of two dimensional figure.

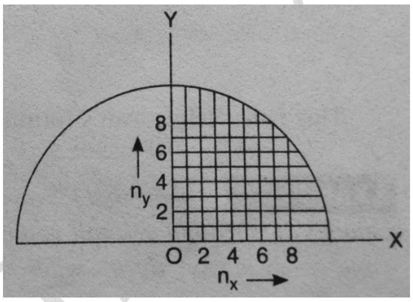
$$\left(n_x^2 + n_y^2\right) = \left(\frac{2l}{\lambda}\right)^2$$

This is the equation of circle.

Here, the total no. of modes of vibration = the total no. of possible sets of (n_x, n_y)

This is also equal to the no. of intersections of positive value of $n_x \,\&\, n_y$ and this is equal to the area of the circle with positive co-ordinates.

No. of modes of vibration $= \frac{1}{4} x\ area\ of\ circle = \frac{1}{4} x\, \pi \left(\frac{2l}{\lambda}\right)^2$



Similarly, in 3- Dimension

No. of modes of vibration = No. of intersections of positive value of $n_x, n_y \,\&\, n_z$. This is equal to the volume of the sphere with positive co-ordinates.

No. of modes of vibration upto wave length λ is (f) $= \frac{1}{8} x\ volume\ of\ sphere = \frac{1}{8} x\ \frac{4}{3}\pi \left(\frac{2l}{\lambda}\right)^3$

$f = \frac{4}{3}\pi\ \frac{l^3}{\lambda^3}$ (or) $f = \frac{4}{3}\pi\ \frac{V}{\lambda^3}$ Here $V = l^3 = Volume\ of\ the\ black\ body$

No. of modes of vibration per unit volume $f = \frac{4}{3}\pi\ \frac{1}{\lambda^3}$

No. of modes of vibration in the range from λ to (λ + d λ) is given by the differential of the above equation. $d\,(f) = \frac{4}{3}\pi\,[\,d\left(\frac{1}{\lambda^3}\right)] = \frac{4}{3}\pi(-3)\left(\frac{1}{\lambda^4}\right)d\lambda$

$df = 4\pi\left(\frac{1}{\lambda^4}\right)d\lambda$ Negative sign is neglected.

Since the waves are transverse, they have 2 polarizations each mode.

$$\therefore\ df = \left(\frac{8\pi}{\lambda^4}\right)d\lambda$$

As per the <u>law of equi-partition of energy</u>, each mode has an average energy ‘kT’.

Here k = Boltzmann’s constant and T = Absolute temperature.

The energy distribution emitted by the black body

$E_\lambda d\lambda =$ No. of modes of vibration X average energy of mode

$$E_\lambda d\lambda = df\,.kT \quad \text{(or)} \quad E_\lambda d\lambda = \left(\frac{8\pi}{\lambda^4}\right)d\lambda\,.kT$$

$$\boxed{\therefore\ E_\lambda d\lambda = \frac{8\pi KT}{\lambda^4}\,d\lambda}$$

This is the Rayleigh-Jean’s formula for energy distribution per unit volume.

Planck’s radiation law

Assumptions

1. Black body contains simple harmonic oscillators all possible frequencies.
2. Emission or absorption of energy take place in discrete amounts. Energy is quantized.
3. The possible values of energy $\varepsilon = nh\nu$ where n = 0, 1, 2, 3, … h = Planck’s constant.

Average energy of an oscillator

Let N_0, N_1, N_2, N_3 … be the no. of oscillators of energies 0, ε, 2ε, 3ε .....respectively.

The average energy of an oscillator $\bar{\varepsilon} = \frac{Total\ energy}{Total\ no.\ of\ particles} = \frac{E}{N} \longrightarrow (1)$

$N = N_0 + N_1 + N_2 + N_3 \ldots + N_r \ldots\ldots \longrightarrow (2)$

$E = 0.\ N_0 + \varepsilon.\ N_1 + 2\varepsilon.\ N_2 + 3\varepsilon.N_3 \ldots\ldots + r\varepsilon.N_r \ldots \longrightarrow (3)$

According to Maxwell’s distribution formula

$$N_r = N_0.e^{(\frac{-r\varepsilon}{kT})} \longrightarrow (4)$$

$$\therefore\ N = N_0 + N_0.e^{(\frac{-\varepsilon}{kT})} + N_0.e^{(\frac{-2\varepsilon}{kT})} + \ldots\ldots N_0.e^{(\frac{-r\varepsilon}{kT})} + \ldots$$

$$N = N_0(1 + e^{(\frac{-\varepsilon}{kT})} + e^{(\frac{-2\varepsilon}{kT})} + \ldots\ldots + e^{(\frac{-r\varepsilon}{kT})} + \ldots)$$

$$\boxed{N = \frac{N_0}{[1-e^{(-\frac{\varepsilon}{kT})}]}} \longrightarrow (4) \qquad \because\ 1 + x + x^2 + x^3 \ldots. = \frac{1}{1-x}$$

Similarly substituting the N_r value in equation (3).

$$E = 0.N_0 + \varepsilon.N_0.e^{(\frac{-\varepsilon}{kT})} + 2\varepsilon.N_0.e^{(\frac{-2\varepsilon}{kT})} + \ldots\ldots + r\varepsilon.N_0.e^{(\frac{-r\varepsilon}{kT})} + \ldots$$

$$E = \varepsilon.N_0.e^{(\frac{-\varepsilon}{kT})}\{1 + +2.N_0.e^{(\frac{-\varepsilon}{kT})} + \ldots\ldots + r.N_0.e^{(\frac{-(r-1)\varepsilon}{kT})} + \ldots\}$$

$$\boxed{E = \varepsilon.N_0.e^{(\frac{-\varepsilon}{kT})}\frac{1}{[1-e^{(-\frac{\varepsilon}{kT})}]^2}} \longrightarrow (5)$$

$$\because\ 1 + 2x + 3x^2 + 4x^3 \ldots. = \frac{1}{(1-x)^2}$$

Substituting eqns. (4) & (5) in eqn. (1)

$$\bar{\varepsilon} = \frac{E}{N} = \left. \varepsilon.N_0.e^{(\frac{-\varepsilon}{kT})}\frac{1}{[1-e^{(-\frac{\varepsilon}{kT})}]^2} \middle/ \frac{N_0}{[1-e^{(-\frac{\varepsilon}{kT})}]} \right.$$

(or) $$\bar{\varepsilon} = \frac{\varepsilon.e^{(\frac{-\varepsilon}{kT})}}{1-e^{(-\frac{\varepsilon}{kT})}}$$

Multiplying the numerator and denominator by $e^{(\frac{\varepsilon}{kT})}$

$$\bar{\varepsilon} = \frac{\varepsilon.e^{(\frac{-\varepsilon}{kT})}}{1-e^{(-\frac{\varepsilon}{kT})}}\ x\ \frac{e^{(\frac{\varepsilon}{kT})}}{e^{(\frac{\varepsilon}{kT})}} = \frac{\varepsilon}{e^{(\frac{\varepsilon}{kT})}-1}$$

$$\boxed{\bar{\varepsilon} = \frac{hc}{\lambda . e^{\left(\frac{hc}{\lambda kT}\right)} - 1}} \qquad \because \ \varepsilon = h\nu = h.\frac{c}{\lambda}$$

This is the average energy of an oscillator.

But we know that the no. of oscillators per unit volume in the range λ to λ+dλ $= \left(\frac{8\pi}{\lambda^4}\right) d\lambda$

(This is the no. of modes of vibration in Rayleigh-Jean's law)

So, the total energy in the range λ to λ+dλ = No. of oscillators per unit volume in the range λ to λ+dλ X Average energy of an oscillator.

i.e. $$E_\lambda d\lambda = \frac{8\pi}{\lambda^4} \, d\lambda . \frac{hc}{\lambda . e^{\left(\frac{hc}{\lambda kT}\right)} - 1}$$

$$\boxed{\therefore \ E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{\left[e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right]} . d\lambda}$$

This is the Planck's formula for energy distribution per unit volume.

<u>Wein's law from Plank's law</u>

Plank's formula is $$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{\left[e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right]} . d\lambda$$

For shorter wave lengths, λ is very small.

So, $e^{\left(\frac{hc}{\lambda kT}\right)} \gg 1$ and one can be neglected. Then Plank's formula becomes

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{\left(\frac{hc}{\lambda kT}\right)}} . d\lambda$$

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} e^{\left(-\frac{hc}{\lambda kT}\right)} . d\lambda$$

Put $8\pi hc = A$ and $\frac{hc}{k} = B$. A & B are constants.

$$\boxed{E_\lambda d\lambda = \frac{A}{\lambda^5} e^{\left(-\frac{B}{\lambda T}\right)} . d\lambda}$$

This is wein's formula. This agrees with experimental values for shorter wave lengths.

<u>Rayleigh -Jean's law from Plank's law</u>

Plank's formula is $$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{1}{\left[e^{\left(\frac{hc}{\lambda kT}\right)} - 1\right]} . d\lambda$$

For longer wave lengths, λ is very large.

So, $e^{\left(\frac{hc}{\lambda kT}\right)} = 1 + \frac{hc}{\lambda kT} + \left(\frac{hc}{\lambda kT}\right)^2 + \left(\frac{hc}{\lambda kT}\right)^3 + \ldots\ldots$

As λ is very large, the higher order terms are neglected.

Then $$e^{\left(\frac{hc}{\lambda kT}\right)} = 1 + \frac{hc}{\lambda kT}$$

Substituting this eqn. in Plank's formula.

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{\left[1+\frac{hc}{\lambda kT}-1\right]}.d\lambda = \frac{8\pi hc}{\lambda^5}\frac{1}{\left[\frac{hc}{\lambda kT}\right]}.d\lambda$$

$$\boxed{E_\lambda d\lambda = \frac{8\pi KT}{\lambda^4}\, d\lambda}$$

This is Rayleigh - Jean's formula. This agrees with experimental values for longer wave lengths.

Pyrometers

Definition :- Pyrometers are the instruments to measure very high temperatures using the laws of thermal radiation.

There are two types of pyrometers 1. Total radiation pyrometers 2. Spectral pyrometers.

Total radiation pyrometer:- This instrument measures the total radiation emitted by a body.

In this the temperature is calculated by using Stefan's law.

Optical (or) spectral pyrometer :- This instrument compares the radiation of particular wave length emitted by a body to that of the radiation of same wave length emitted by a standard body.

In this the temperature is calculated by using Wein's displacement law.

Advantages of pyrometers

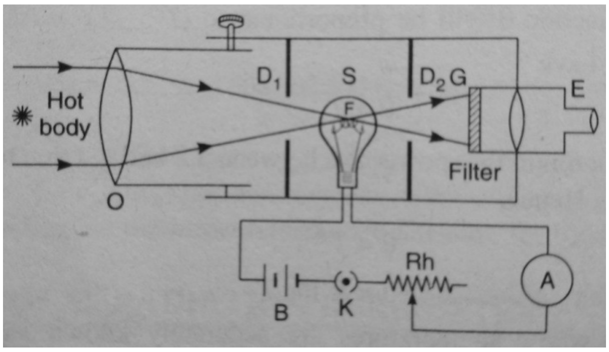
1. These are used to measure very high temperatures.
2. The body may be at infinite distance.
3. The body may not be in contact.
4. Any temperature can be measured by extrapolating the graphs of radiation laws.

Disadvantages of pyrometers

1. The minimum temperature to be measured with pyrometer is 600^0C.
2. The measured temperature with pyrometer is always less than the actual value.

Disappearing filament optical pyrometer

Construction :-



- ❖ This pyrometer consists of a telescope having two tubes moving in one another by rock-pinion adjustment.
- ❖ To the 1st end of the 1st tube an objective O, is fixed. To the 2nd end of the 2nd tube an eye-piece E, is fixed.
- ❖ The cross wires are replaced by an electric bulb S. The filament of the bulb is connected to a battery B, plug key K, rheostat Rh and ammeter A, in series.
- ❖ A red filter is arranged in front of the eye-piece and two diaphragms D_1 and D_2 are arranged before and after the bulb.

Working

- First the pyrometer is placed such that the objective is facing the hot body whose temperature is to be measured.
- By rock-pinion adjustment the image of the hot body is made to focus on the filament of the bulb. The image of the filament and the image of the hot body are viewed by the eye-piece, through the red filter back ground.
- Now the current is sent through the filament by switching on the plug key and the current is varied by adjusting the rheostat until the filament disappears in the back-ground.
- The current I, is measured with the ammeter.

Calculation

- The temperature of the hot body T, is calculated using the formula

$$\boxed{I = a + bT + c\,T^2}$$

Here a, b and c are constants.

To know these constants, first the currents are measured for three known temperatures of three different bodies. By substituting the three sets of I, T values in the above equation, we get 3 equations. By solving these 3 equations we will get the values of the constants a, b and c.

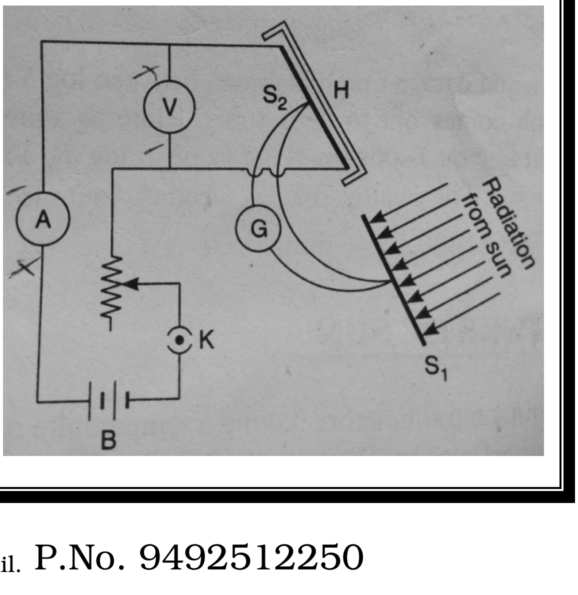
By using this pyrometer the temperatures between 600°C – 1500°C can be measured. The upper limit can be increased by using rotating sector.

Solar constant

Definition :- It is the amount of solar energy is received by a black surface per unit area per unit time when the surface is placed, normal to the Sun rays and at the mean distance of the earth from the Sun in the absence of earth's atmosphere.
The solar constant value is 1340 W/m^2.

Determination of solar constant – Angstrom's phyrheliometer

Construction



- ∗ This phyrheliometer consists of two identically equal blackened platinum strips S_1, S_2.
- ∗ These two strips are placed normal to the Sun rays. S_1 is open to receive the radiation from the Sun. S_2 is covered with double walled shield H.
- ∗ The back sides of the two strips are connected to the two junctions of a thermo couple through a galvanometer.
- ∗ The strip S_2 is connected to an electrical

circuit. In the circuit a battery, plug-key, ammeter and rheostat are connected in series and voltmeter is connected in parallel.

Working

- If the two strips S_1, S_2 are uncovered, they both exposed to Sun radiation. Then the two strips or the two junctions of thermocouple are at the same temperature and no deflection is observed in the galvanometer.
- If the strip S_2 is covered with the shield H, then the strip S_1 is at higher temperature and the strip S_2 is at lower temperature & the galvanometer shows deflection.
- Now the current is sent through the circuit and is adjusted by using rheostat until the galvanometer shows zero deflection. Then note the voltage V and current I values.
- At this stage the two strips are at the same temperature i.e. both strips receive the same quantity of heat.

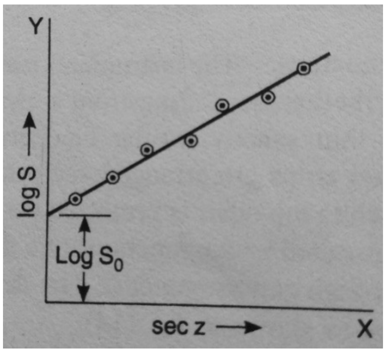
Heat received by S_1 from Sun = Heat received by S_2 from the circuit.

S.A.a. = V.I.

Here S = Solar constant A = Area of the front surface of S_1 & a = Absorption coefficient of S_1.

The solar constant, S value can be calculated from

$$\boxed{\therefore\ S = \frac{V.I}{A.a}}$$



The experiment is repeated through out the year for different zenith angles. The average solar constants through out the year for different zenith angles are calculated.

The actual solar constant S_0 can be calculated from the relation $S = S_0\,\tau^{\sec z}$

Here τ = Transmission coefficient of the atmosphere

Z = Zenith angle

Taking logarithms on both sides for the above equation. $\log S = \log S_0 + \sec z\,.\log\tau$

A graph is drawn by taking log S on Y-axis and sec z on X-axis. The intercept on Y-axis gives $\log S_0$ from this S_0 can be calculated.

The value comes out as 1,340 W/m^2.

Temperature of Sun

Consider the Sun as the perfect black body and the solar constant value is 1,340 W/m^2.

Let the radius of the photosphere of the Sun = R

Surface area of the Sun = $4\pi R^2$

Energy emitted from the surface of the Sun per unit time = $4\pi R^2.\sigma T^4 \longrightarrow$ (1)

T= temperature of the Sun From Stefan's law

The same energy is spread in all directions from the Sun.

Distance between the Sun and earth = r

Surface area of the sphere of radius r = $4\pi r^2$

Energy received per unit area per unit time = Solar constant S

Energy received on the surface area of the sphere of radius r = $4\pi r^2.\ S \longrightarrow$ (2)

Eqns. (1) and (2) are equal.

$$4\pi r^2.\ S = 4\pi R^2.\sigma T^4$$

$$T^4 = \left(\frac{r}{R}\right)^2.\frac{S}{\sigma} \quad \text{or} \quad \boxed{T = \left[\left(\frac{r}{R}\right)^2.\frac{S}{\sigma}\right]^{\frac{1}{4}}}$$