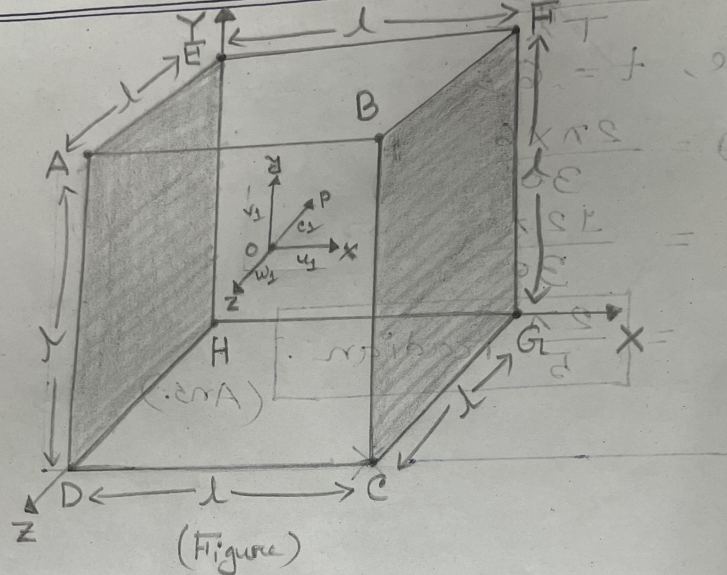


Week

3. (Kinetic Theory of Gases)

- Expression for the pressure of a Gas :-



We consider a cubical vessel ABCDEFGH of side 'l' cm containing the gas.

The volume of the vessel of the gas, $V = l^3$ cc. Let 'n' and 'm' represent the very large number of molecules present in the vessel and the mass of each molecule respectively.

Consider a molecule 'P' moving in a random direction with a velocity c_1 . The velocity of molecule along X, Y, Z axes three perpendicular direction which is u_1 , v_1 and w_1 . Therefore,

$$c_1^2 = u_1^2 + v_1^2 + w_1^2$$

Let the molecule strike the face BCGF is u_1 and the momentum of the molecule is mu_1 . This molecule is reflected back with the opposite face ADHE is $-u_1$ and the momentum is $-mu_1$.

$$\therefore \text{The change of momentum} = mu_1 - (-mu_1) \\ = mu_1 + mu_1 \\ = 2mu_1$$

As the velocity of the molecule is u_1 , the time interval between two successive impacts on the wall BCGF is

$$= \frac{2l}{u_1} \text{ seconds.} \quad \left[\because s = vt \mid s = l + l = 2l \right. \\ \left. \Rightarrow t = \frac{s}{v} \mid v = u_1 \right]$$

Therefore, rate of change of momentum is

$$F_x = \frac{2mu_1}{\frac{2l}{u_1}} \quad \left[\because F = \frac{mv}{t} \right]$$

$$= \frac{mu_1^2}{l}$$

$$\therefore P_x = \frac{F_x}{A} = \frac{\frac{mu_1^2}{l}}{l^2} = \frac{mu_1^2}{l \times l^2} = \frac{mu_1^2}{l^3}$$

$$\Rightarrow P_x = \frac{m}{l^3} (u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2)$$

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Similarly the pressure P_y on the walls ABFE and CDGH is given by

$$\therefore P_y = \frac{m}{l^3} (v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2)$$

and the pressure P_z on the walls ABCD and EFGH is given by

$$\therefore P_z = \frac{m}{l^3} (w_1^2 + w_2^2 + w_3^2 + \dots + w_n^2)$$

$\therefore$ The mean pressure P is given by

$$P = \frac{P_x + P_y + P_z}{3}$$

$$= \frac{m}{3l^3} \left[(u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2) + (v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2) + (w_1^2 + w_2^2 + w_3^2 + \dots + w_n^2) \right]$$

$$= \frac{m}{3l^3} [c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2] \quad (1)$$

The ~~root~~-mean-square-velocity of the molecules

$$c^2 = \frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2}{n}$$

$$\Rightarrow n c^2 = c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2$$

Putting this value in equation (1), we get

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$$P = \frac{1}{3} \frac{m n c^2}{V} \quad [\because V = l^3] \quad \text{--- (2)}$$

But $M = m n$ where 'M' is the mass of the gas of volume V, 'm' is the mass of each molecule and 'n' is the number of molecules in a volume V.

$$\therefore P = \frac{M c^2}{3V}$$

$$\Rightarrow P = \frac{1}{3} M c^2 \quad \text{--- (3)}$$

Equation (3) is pressure force per unit volume where 'M' mass of the gas.

again,

$$\rho = \frac{M}{V}$$

Where,

ρ = the density of the gas

M = Mass of the gas

V = Volume of the gas

$$\therefore P = \frac{1}{3} \rho c^2$$

$$\Rightarrow c^2 = \frac{3P}{\rho}$$

Here 'c' is root mean square velocity.

$$\therefore c = \sqrt{\frac{3P}{\rho}}$$

$$PV = \frac{1}{3} m n c^2$$

$$PV = \frac{1}{3} M c^2$$

$$P = \frac{1}{3} m n c^2 \quad [\text{per unit volume}]$$

2nd week

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Kinetic Energy per unit Volume of a gas —

We know,

$$PV = \frac{1}{3} M c^2$$

$$\Rightarrow P = \frac{1}{3} \cdot \frac{M}{V} \cdot c^2$$

$$\Rightarrow P = \frac{1}{3} \rho c^2$$

$$\Rightarrow \frac{1}{2} P = \frac{1}{3} \times \frac{1}{2} \rho c^2$$

$$\Rightarrow \frac{1}{2} \rho c^2 = \frac{3}{2} P$$

$$\Rightarrow E = \frac{3}{2} P \quad [\because E = \frac{1}{2} \rho c^2]$$

$$\Rightarrow P = \frac{2}{3} E$$

where $E = \frac{1}{2} \rho c^2$ is equal to the kinetic energy per unit volume of the gas. ρ is the mass per unit volume.

Hence, the pressure of a gas is numerically equal to two-thirds of the mean kinetic energy of translation of a unit volume of the molecules.

Kinetic Interpretation of Temperature (T) -

We know, the pressure of a gas from kinetic theory is,

$$P = \frac{1}{3} \rho c^2$$

$$\Rightarrow P = \frac{1}{3} \frac{M}{V} c^2$$

$$\Rightarrow PV = \frac{1}{3} M c^2$$

For 1 gm molecule of the gas at a temperature T (K)

$$PV = RT \quad [\because PV = nRT; n=1]$$

$$\Rightarrow \frac{1}{3} M c^2 = RT$$

$$\Rightarrow \frac{1}{3} \times \frac{1}{2} \times M c^2 = \frac{1}{2} RT$$

$$\Rightarrow \frac{1}{2} M c^2 = \frac{3}{2} RT$$

Let m is the mass of each molecule and N is Avogadro's number.

$$M = m \times N$$

$$\Rightarrow \frac{1}{2} m N c^2 = \frac{3}{2} RT$$

$$\Rightarrow \frac{1}{2} m c^2 = \frac{3}{2} \frac{R}{N} T$$

$$\therefore \frac{1}{2} m c^2 = \frac{3}{2} kT$$

$$\Rightarrow E = \frac{3}{2} kT$$

where $k = \frac{R}{N}$ is Boltzmann's constant.

Therefore, kinetic energy of each gas molecule is directly proportional to absolute temperature. $E \propto T$.

Degress of freedom and maxwell's law of Equipartition of Energy

Maxwell's law: For each degress of freedom the kinetic energy of each molecule of gas is same.

We know,

According to the kinetic theory of gases,

$$\frac{1}{2} m c_1^2 = \frac{3}{2} kT$$

But,

$$c_1^2 = u_1^2 + v_1^2 + w_1^2$$

and,

$$u_1 = v_1 = w_1$$

or,

$$\frac{1}{2} m (u_1^2 + v_1^2 + w_1^2) = \frac{3}{2} kT$$

$$\Rightarrow \frac{1}{2} m (u_1^2 + u_1^2 + u_1^2) = \frac{3}{2} kT$$

$$\Rightarrow \frac{1}{2} m \times 3u_1^2 = \frac{3}{2} KT$$

$$\Rightarrow \frac{1}{2} m u_1^2 = \frac{1}{2} KT$$

Similarly,

$$\therefore \frac{1}{2} m v_1^2 = \frac{1}{2} KT$$

$$\therefore \frac{1}{2} m w_1^2 = \frac{1}{2} KT$$

Therefore, Kinetic energy for each degree of freedom is $\frac{1}{2} KT$.

X

* Specific Heat - The quantity of heat required to raise the temperature of one gram of a substance by one celsius degree is called specific heat.

* C_p → At constant pressure, the quantity of heat required to raise the temperature of one gram of a substance by one celsius degree is called specific heat. (C_p)

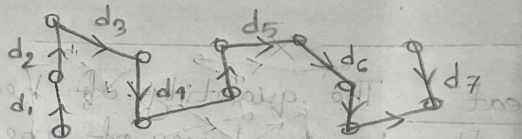
* C_v → At constant volume, the quantity of heat required to raise the temperature of one gram of a substance by one celsius degree is called specific heat at constant volume. (C_v)

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

X

- Mean free Path - The path covered by a molecule between any two consecutive collisions in a straight line and is called the free path. After a number of collisions the total path appears to be zig-zag and the free path is not constant. If the total distance is S travelled after N collisions the ~~the~~ mean free path is

$$\lambda = \frac{S}{N}$$



$$\lambda = \frac{d_1 + d_2 + \dots + d_n}{n}$$

$$\therefore \lambda = \frac{\sum d}{n}$$

$$\lambda = \frac{1}{\pi d^2 n} \quad (\text{Clausius})$$

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n} \quad (\text{Maxwell})$$

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

$$\lambda = \frac{C_p}{C_v} \times \dots$$

(Example)

(5.23) Calculate the mean free path of a gas molecule given that the molecule diameter is $2 \times 10^{-8} \text{ cm}$ and the number of molecule per cc is 3×10^{19} .

⇒ We know,

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

$$= \frac{1}{3.14 \times (2 \times 10^{-8})^2 \times 3 \times 10^{19}}$$

$$= 2.65 \times 10^5 \text{ cm}$$

$$\therefore \lambda = 2.65 \times 10^5 \text{ cm}$$

Here,

$$d = 2 \times 10^{-8} \text{ cm}$$

$$n = 3 \times 10^{19}$$

(5.24) Calculate the mean free path of gas molecule in a chamber of 10^{-8} mm of mercury pressure assuming the molecule diameter to be $2 \text{ \AA}$.
273K and 760mmHg the number of molecule in 22.4 litres of a gas 6.023×10^{23}

$$\Rightarrow n = \frac{6.023 \times 10^{23} \times 10^{-3}}{22.4 \times 760}$$

$$= 3.538 \times 10^{19} \text{ molecules/cm}^3$$

$$d = 2 \text{ \AA} = 2 \times 10^{-8} \text{ cm}$$

Mean free path,

$$\lambda = \frac{1}{\pi d^2 n} = \frac{1}{3.14 \times (2 \times 10^{-8})^2 \times 3.538 \times 10^{19}}$$

$$= 2.25 \times 10^5 \text{ cm} \quad (\text{Ans.})$$

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(Examples.)

(5.4) Calculate the number of molecules in one c.c. of oxygen at N.T.P. using the following data

$\rho = 13.6 \text{ g/cm}^3$ (mercury)

R.M.S. velocity of oxygen molecules at $0^\circ \text{C} = 4.62 \times 10^4 \text{ cm/s}$

Mass of one molecule of oxygen = $52.8 \times 10^{-24} \text{ g}$

$\Rightarrow$ We know,

$$P = \frac{1}{3} \rho c^2$$

$$= \frac{1}{3} \times 13.6 \times (4.62 \times 10^4)^2$$

$$= 1017416.4 \text{ dyne/cm}^2$$

again,

$$P = \frac{1}{3} m n c^2$$

$$\Rightarrow 3P = m n c^2$$

$$\Rightarrow n = \frac{3P}{m c^2}$$

$$\Rightarrow n = \frac{3 \times 1017416.4}{52.8 \times 10^{-24} \times (4.62 \times 10^4)^2}$$

$$= 2.7 \times 10^{19} \text{ s} = \text{Ans.}$$

Here,

$$\rho = 13.6 \text{ g/cm}^3$$

$$c = 4.62 \times 10^4 \text{ cm/s}$$

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

$$R = 0.0821 \text{ L atm/mol.K}$$

$$T = 273 \text{ K}$$

$$M = 32 \text{ g/mol (O}_2\text{)}$$

$$P = 1 \text{ atm} = 1.013 \times 10^6 \text{ dyne/cm}^2$$

$$m = 52.8 \times 10^{-24} \text{ g}$$

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(b) At what Celsius temperature will oxygen molecules have the same root-mean-square velocity as that of hydrogen molecules at -100°C ?

⇒ We know,

The energy of a gas molecule is,

$$\frac{1}{2} m c^2 = \frac{3}{2} k T$$

For hydrogen molecules,

$$\frac{1}{2} m_1 c_1^2 = \frac{3}{2} k T_1 \quad \text{--- (i)}$$

For Oxygen molecules,

$$\frac{1}{2} m_2 c_2^2 = \frac{3}{2} k T_2 \quad \text{--- (ii)}$$

Dividing (i) by (ii)

$$\frac{m_1 c_1^2}{m_2 c_2^2} = \frac{T_1}{T_2} \quad \text{--- (iii)}$$

Hence,

$$c_1 = c_2$$

$$T_1 = -100^{\circ}\text{C} = -100 + 273 = 173 \text{ K}$$

$$T_2 = ?$$

$$\frac{m_1}{m_2} = \frac{1}{16} \Rightarrow \frac{m_2}{m_1} = 16$$

From equation (iii)

$$T_2 = \frac{T_1 \times m_2}{m_1} = \frac{m_2}{m_1} \times T_1 = 16 \times 173 = 2768 \text{ K}$$

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$$\Rightarrow T_2 = 2768 - 273 = 2495^\circ\text{C} \quad (\text{Ans.})$$

(5.7) Calculate the volume occupied by 3.2 grams of oxygen at 76 cm of Hg and 27°C .

$\Rightarrow$ Here,

$$P = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$T = 27 + 273 = 300\text{K}$$

$$R = 8.31 \times 10^7 \text{ ergs/gmol}\cdot\text{K}$$

We know,

$$PV = RT$$

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

$$= \frac{8.31 \times 10^7 \times 300}{76 \times 13.6 \times 980}$$

$$= 24611.8 \text{ cc per gmol}$$

Volume for 3.2 g. of oxygen = v

$$= \frac{24611.8 \times 3.2}{32}$$

$$= 2461 \text{ cc}$$

(Ans.)

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(5.9) Calculate the number of molecules in one cubic metre of an ideal gas at N.T.P.

⇒ Let the number of molecules per cc be n .

$$n = \frac{PN}{RT}$$

Number of molecules in one cubic metre volume,

$$x = n \times 10^6$$

$$\Rightarrow x = \frac{PN}{RT} \times 10^6$$

Here,

$$P = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$N = 6.023 \times 10^{23}$$

$$R = 8.31 \times 10^7 \text{ erg/g mol-K}$$

$$T = 273 \text{ K}$$

$$\therefore x = \frac{76 \times 13.6 \times 980 \times 6.023 \times 10^{23} \times 10^6}{8.31 \times 10^7 \times 273}$$

$$= 2.68 \times 10^{25}$$

(Ans.)

(5.10) Calculate the number of molecules in one litre of an ideal gas at 136.5°C temperature and 3 atmospheres pressure.

$\Rightarrow$ Let, the number of molecules per cc =

$$\therefore n = \frac{PN}{RT}$$

Number of molecules in one litre,

$$x = n \times 10^3$$

$$\Rightarrow x = \frac{PN \times 10^3}{RT}$$

Here,

$$P = 3 \times 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$N = 6.023 \times 10^{23}$$

$$R = 8.31 \times 10^7 \text{ ergs/g mol} \cdot \text{K}$$

$$T = 136.5 + 273 = 409.5 \text{ K}$$

$$\therefore x = \frac{76 \times 13.6 \times 980 \times 3 \times 6.023 \times 10^{23} \times 10^3}{8.31 \times 10^7 \times 409.5}$$

$$= 5.378 \times 10^{22}$$

(Ans.)

(Ans.)

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erature

$c = n$

(5.11)

Calculate the number of molecules per cc of the gas. The number of molecules per cc of a gas is 2.7×10^{19} at N.T.P.

- (i) at 0°C and 10^{-6} mm pressure of mercury
- (ii) at 39°C and 10^{-6} mm pressure of mercury.

$\Rightarrow$ We know,

for a unit of volume of gas,

$$P = \frac{1}{3} n m c^2$$

(i) at 0°C ,

$$P_1 = \frac{1}{3} n_1 c^2 \quad \text{--- (i)}$$

at 0°C and 10^{-6} mm pressure,

$$P_2 = \frac{1}{3} n_2 c^2 \quad \text{--- (ii)}$$

From (i) and (ii)

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$\Rightarrow n_2 = \frac{n_1 P_2}{P_1}$$

Here,

$$n_1 = 2.7 \times 10^{19}$$

$$P_1 = ~~76 \times 13.6 \times 980~~ \text{ dynes/cm}^2 \quad 760 \text{ mm Hg}$$

$$P_2 = 10^{-6} \text{ mm of Hg}$$

$$= ~~10^{-7} \text{ cm of Hg}~~

$$= ~~10^{-7} \times 13.6 \times 980~~ \text{ dynes/cm}^2$$$$

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$$\therefore n_2 = \frac{2.7 \times 10^{19} \times 10^{-1} \times 19.6 \times 980 \times 10^{-6}}{76 \times 19.6 \times 980 \times 760}$$

$$= 3.553 \times 10^{10}$$

(ii) at 39°C ,

$$p = \frac{1}{3} m n_2 c_2^2 \quad \text{--- (i)}$$

at 39°C and 10^{-6} mm of Hg pressure

$$p = \frac{1}{3} m n_3 c_3^2 \quad \text{--- (ii)}$$

Here p is same in both cases.

$$\therefore \frac{1}{3} m n_2 c_2^2 = \frac{1}{3} m n_3 c_3^2$$

$$\therefore n_2 c_2^2 = n_3 c_3^2$$

$$\Rightarrow \frac{n_2}{n_3} = \frac{c_3^2}{c_2^2}$$

But,

$$c \propto \sqrt{T}$$

$$\therefore \frac{c_3}{c_2} = \sqrt{\frac{T_3}{T_2}}$$

$$\Rightarrow \frac{c_3}{c_2} = \sqrt{\frac{T_3}{T_2}}$$

$$\therefore n_3 = \frac{n_2 \times T_2}{T_3}$$

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Here,

$$n_2 = 3.553 \times 10^{10}$$

$$T_2 = 0^\circ\text{C} = 273\text{K}$$

$$T_3 = 39^\circ\text{C} = 39 + 273 = 312\text{K}$$

$$\therefore n_3 = \frac{3.553 \times 10^{10} \times 273}{312}$$
$$= 3.109 \times 10^{10}$$

(Ans.)

(5.13) Calculate the average kinetic energy of a molecule of gas at a temperature of 300K .

$\Rightarrow$ We know,
Average kinetic Energy of a molecule,

$$\frac{1}{2} m \bar{c}^2 = \frac{3}{2} k T$$

Here,

$$k = 1.38 \times 10^{-16} = \frac{8.31 \times 10^7 \text{ (R)}}{6.023 \times 10^{23} \text{ (N)}}$$

$$T = 300\text{K}$$

$$\therefore \frac{1}{2} m \bar{c}^2 = \frac{3}{2} \times 1.38 \times 10^{-16} \times 300$$

$$= 6.21 \times 10^{-14} \text{ ergs.}$$

(Ans.)

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(5.11) Calculate the mean translational kinetic energy per molecule of a gas at 727°C , given $R = 8.32 \text{ joules/mol}\cdot\text{K}$.

$\Rightarrow$ Here,

$$N = 6.023 \times 10^{23}$$

$$T = 727 + 273 = 1000 \text{ K}$$

$$R = 8.32 \text{ joules/mol}\cdot\text{K}$$

$$\therefore k = \frac{R}{N} = \frac{8.32}{6.023 \times 10^{23}} = 1.38 \times 10^{-23} \text{ joules/molecule}\cdot\text{K}$$

$\therefore$ Mean translational kinetic energy per molecule $= \frac{3}{2} kT$

$$= \frac{3 \times 1.38 \times 10^{-23} \times 1000}{2}$$

$$= 2.07 \times 10^{-20} \text{ Joule}$$

(Ans.)

(5.29) At what temperature, pressure remaining constant will be r.m.s. velocity of a gas be half its value at 0°C ?

$\Rightarrow$ We know,

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$$\frac{c_2}{c_1} = \sqrt{\frac{T_2}{T_1}}$$

Here,

$$c_2 = \frac{c_1}{2} \quad (\text{condition})$$

$$T_2 = ?$$

$$T_1 = 273 \text{ K}$$

$$\therefore \frac{\frac{c_1}{2}}{c_1} = \sqrt{\frac{T_2}{273}}$$

$$\Rightarrow \frac{c_1}{2} \times \frac{1}{c_1} = \sqrt{\frac{T_2}{273}}$$

$$\Rightarrow \frac{1}{2} = \sqrt{\frac{T_2}{273}}$$

$$\Rightarrow \frac{1}{4} = \frac{T_2}{273}$$

$$\Rightarrow T_2 = \frac{273}{4} = 68.25 \text{ K}$$

$$\therefore T_2 = 68.25 - 273 = -204.75^\circ \text{C}$$

(Ans.)

~~_____ X _____~~

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putting this values in equation (6) $\Rightarrow$

$$1 \cdot \left(\frac{\partial T}{\partial y}\right)_x - 0 \cdot \left(\frac{\partial P}{\partial y}\right)_x = 0 \cdot \left(\frac{\partial T}{\partial x}\right)_y - 1 \cdot \left(\frac{\partial P}{\partial x}\right)_y$$

$$\Rightarrow \left(\frac{\partial T}{\partial y}\right)_x = - \left(\frac{\partial P}{\partial x}\right)_y$$

$$\Rightarrow \left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial s}\right)_v$$

$$\Rightarrow \left(\frac{\partial T}{\partial v}\right)_s = - \left(\frac{\partial P}{\partial H}\right)_v \quad \left[\because \partial s = \frac{\partial H}{T} \right]$$

$$\Rightarrow \left(\frac{\partial T}{\partial v}\right)_s = - T \left(\frac{\partial P}{\partial H}\right)_v$$

[Proved]

(iii) Let $s = x$, $T = y$

$$\left(\frac{\partial s}{\partial x}\right)_y = 1 \quad , \quad \left(\frac{\partial T}{\partial y}\right)_x = 1$$

$$\left(\frac{\partial s}{\partial y}\right)_x = 0 \quad , \quad \left(\frac{\partial T}{\partial x}\right)_y = 0$$

putting this values in equation (6) $\Rightarrow$

$$1 \cdot 1 - \left(\frac{\partial v}{\partial x}\right)_y \cdot \left(\frac{\partial P}{\partial y}\right)_x = 0 \cdot 0 - \left(\frac{\partial v}{\partial y}\right)_x \cdot \left(\frac{\partial P}{\partial x}\right)_y$$

$$\Rightarrow \left(\frac{\partial v}{\partial y}\right)_x \left(\frac{\partial P}{\partial x}\right)_y - \left(\frac{\partial v}{\partial x}\right)_y \left(\frac{\partial P}{\partial y}\right)_x = -1$$

$$\Rightarrow \left(\frac{\partial v}{\partial x}\right)_y \left(\frac{\partial P}{\partial y}\right)_x - \left(\frac{\partial v}{\partial y}\right)_x \left(\frac{\partial P}{\partial x}\right)_y = 1$$

$$\Rightarrow \left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial P}{\partial T}\right)_s - \left(\frac{\partial v}{\partial T}\right)_s \left(\frac{\partial P}{\partial s}\right)_T = 1 \quad [\text{Proved}]$$