

$C_p$  and  $C_v$  calculation:-

(A) Monoatomic gases:-

Total degree of freedom =  $3n$ ;  $n$  = no. of atoms in a molecule

Total degree of freedom =  $3 \times 1 = 3$

Trans. degree of freedom = 3

Total energy;  $E = 3 \times \frac{1}{2} RT$

Total molar energy,  $E = 3 \times \frac{1}{2} RT$

$C_v = \left( \frac{\partial E}{\partial T} \right)_v = \frac{3}{2} R \approx 3 \text{ cal mol}^{-1} \text{ K}^{-1}$

$C_p = C_v + R \approx 5 \text{ cal mol}^{-1} \text{ K}^{-1}$

(B) Diatomic gas:-

Total degrees of freedom,  $F = 3 \times 2 = 6$

Translational degrees of freedom = 3

Energy contribution =  $3 \times \frac{1}{2} RT$

Rotational degrees of freedom = 2

Energy contribution =  $2 \times \frac{1}{2} RT = RT$

Vibrational degrees of freedom = 1

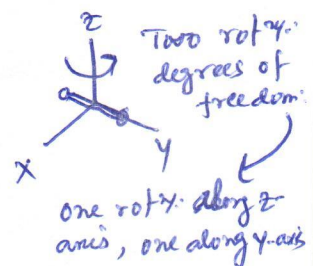
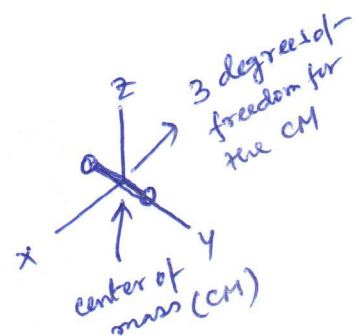
Energy contribution =  $RT$

Total energy =  $\frac{3}{2} RT + RT + RT = \frac{7}{2} RT$

Total Molar energy =  $\frac{7}{2} RT$

$C_v = \left( \frac{\partial E}{\partial T} \right)_v = \frac{7}{2} R \approx 7 \text{ cal mol}^{-1} \text{ K}^{-1}$

$C_p = 9 \text{ cal mol}^{-1} \text{ K}^{-1}$



vibrational motion along the molecular axis.

In general:

Total degrees of freedom;  $F = 3n$

Trans. " " " ;  $F = 3$

Rot. " " " ;  $F = 2$  (linear)  
 $= 3$  (non-linear)

Vib. " " " ;  $F = (3n - 5)$  (linear)

$= (3n - 6)$  (non-linear)

vibrational motion contribution:

$2 \times \frac{1}{2} RT = RT$

Since it has both kinetic and potential energy modes.

..... Kinetic Theory and the Gaseous State

Calculate the  $C_p$  &  $C_v$  values of  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ .

For  $\text{CO}_2$ : Total d.o.f =  $3 \times 3 = 9$

$$\text{Tr. d.o.f} = 3 ; \text{Energy} = \frac{3}{2} kT$$

$$\text{Rot. d.o.f} = 2 ; \text{Energy} = 2 \times \frac{1}{2} kT = kT$$

$$\text{Vib. d.o.f} = (3 \times 3 - 5) = 4 ; \text{Energy} = 4 kT$$

$$\text{Total Energy} = \frac{3}{2} kT + kT + 4 kT = \frac{13}{2} kT$$

$$\text{Molar " } = \frac{13}{2} RT$$

$$C_v = \left( \frac{\partial E}{\partial T} \right)_v = \frac{13R}{2} \approx 13 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$C_p \approx 15 \text{ cal mol}^{-1} \text{ K}^{-1}$$

For  $\text{SO}_2$ : Total d.o.f =  $3 \times 3 = 9$

$$\text{Tr. " } = 3 ; \text{Energy} = \frac{3}{2} kT$$

$$\text{Rot. " } = 3 ; \text{Energy} = \frac{3}{2} kT$$

$$\text{Vib. " } = (3 \times 3 - 6) = 3 ; \text{Energy} = 3 kT$$

$$\text{Total energy} = \frac{3}{2} kT + \frac{3}{2} kT + 3 kT = 6 kT$$

$$\text{Molar " } = 6 RT$$

$$C_v \approx 6R \approx 12 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$C_p \approx 14 \text{ cal mol}^{-1} \text{ K}^{-1}$$

For  $\text{NH}_3$ : - Total d.o.f =  $3 \times 4 = 12$

$$\text{Tr. " } = 3 ; \text{Energy} = \frac{3}{2} kT$$

$$\text{Rot. " } = 3 ; \text{ " } = \frac{3}{2} kT$$

$$\text{Vib. " } = (3 \times 4 - 6) = 6 ; \text{Energy} = 6 kT$$

$$\text{Total energy} = \frac{3}{2} kT + \frac{3}{2} kT + 6 kT = 9 kT$$

$$\text{Molar energy} = 9 RT$$

$$C_v = 9R \approx 18 \text{ cal mol}^{-1} \text{ K}^{-1} ; C_p \approx 20 \text{ cal mol}^{-1} \text{ K}^{-1}$$

Limitations of equipartition principle :-

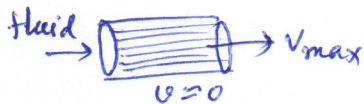
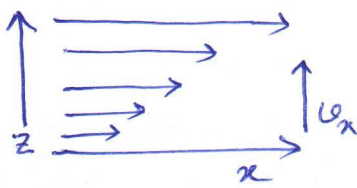
Excluding monoatomic gases  $C_p, C_v$  values calculated on the basis of equipartition principle matches with the experimental values only at high temp.

Reason: - Equipartition principle is derived from Maxwell distribution of molecular speed which is a classical theory. Hence, this principle is not applicable for systems having quantized energy level or in other word having quantized motion like rot. or vib. (i.e. diatomic or polyatomic gases). At high temp; the quantized energy level becomes continuous. As a result calculated  $C_p, C_v$  values based on classical theory matches with the experimental values.



## Viscosity of gases:-

Viscosity is a flowing property associated with liquid and gas, commonly called fluid. When a fluid moves under a low pressure difference, it flows in layer (streamline motion). Top most layer has maximum velocity while bottom most layer adjacent to the solid surface remains almost stationary (no-slip condition). When the flow attains steady state condition, there occurs definite velocity gradient,  $\frac{dv}{dz}$ .



The fluid layers move along  $x$ -axis in  $xy$ -plane and velocity of the layers are increasing along  $z$ -axis. Similarly when a fluid flows in a tube, centre layer has maximum velocity and the layer attached to the walls of the tube has minimum velocity.

Adjacent horizontal layers of fluid flow at different velocities and slide over one another. As the two adjacent layers slip past each other, each exerts a frictional resistive force on the other, and this internal friction gives rise to viscosity. Thus, viscosity is the internal friction developed between two fluid layers moving with unequal velocities. Due to this property, some fluids flow more easily than the others. This property that characterizes a fluid's resistance to flow is called its viscosity.

$f$  = viscous force

$f \propto A$  (Area of contact)

$\propto dv$  (velocity difference of two adjacent layers)

$\propto \frac{1}{dz}$  ( $dz$  = distance between two layers)

Thus,  $f \propto A \frac{dv}{dz}$  ( $\frac{dv}{dz}$  = velocity gradient)

$f = -\eta A \frac{dv}{dz}$  ; - sign indicates that viscous force acts in opposition to the fluid flow.

$\eta$  = viscosity coefficient of the fluid, depends on the nature of the fluid and temperature.

## Definition of viscosity co-efficient:—

$$|f| = \eta A \frac{dv}{dz}$$

$$\therefore A = 1, dv = 1, dz = 1 ; |f| = \eta$$

viscosity co-efficient is defined as the frictional force required to maintain unit difference in velocities betw. two fluid layers of unit contact area and which are unit distance apart.

unit of  $\eta$ :—

$$\eta = |f| \cdot \frac{1}{A} \cdot \frac{dz}{dv}$$

CGS system:

$$= \text{dyne} \cdot \frac{1}{\text{cm}^2} \cdot \frac{\text{cm} \cdot \text{s}}{\text{cm}}$$

$$= \text{dyne} \cdot \text{s} / \text{cm}^2 = \text{Poise (scientist Poiseuille)}$$

SI system:  $\text{Newton} \cdot \text{s} / \text{meter}^2 = \text{Pascal sec (Pa s)}$

$$1 \text{ Pa s} = 1 \text{ N m}^{-2} \text{ s} = 10^5 \text{ dyne} \times (10^2 \text{ cm})^{-2} \text{ sec} = 10 \text{ dyne cm}^{-2} \text{ sec} = 10 \text{ Poise}$$

Dimension of  $\eta$ :—

$$\eta = \frac{f}{A \cdot \frac{dv}{dz}} = \frac{MLT^{-2}}{L^2 \frac{LT^{-1}}{L}} = \frac{M}{LT}$$

Relation betw. viscosity co-eff. and mean free path ( $l$ ):—  
Kinetic theory of gas viscosity.

[Please read from book.]  
Viscosity co-eff. ( $\eta$ ) can be expressed by following eqn., where  
 $l$  = mean free path.

$$\eta = \frac{1}{3} \rho \bar{c} l$$

$$\text{Replacing } \bar{c} = \sqrt{\frac{8RT}{\pi m}} ; l = \frac{1}{\sqrt{2} \pi \sigma^2 n} \text{ and } \rho = nm,$$

$$\text{we will get } \eta = \frac{2}{3} \frac{\sqrt{MRT}}{\pi^{3/2} \sigma^2 N_A} ;$$

Thus, by determining  $\eta$  of a gas at given temp., it is possible to calculate the molecular diameter,  $\sigma$ , of the gas.



### Effect of temp. and Pr. on the viscosity of gases:—

The expression of viscosity of gases from the kinetic model shows that viscosity of a gas increases with increase of temp, and  $\eta \propto \sqrt{T}$

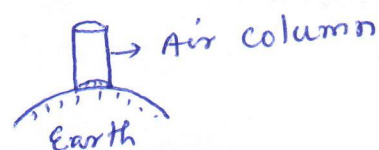
This is qualitatively right and supported by expt. This indicates the success of kinetic model of the gas viscosity.

However, in reality, with increase of temp.,  $\eta$  of the gas increases more than the predicted by the relation. This is due to the assumption of the kinetic theory that the molecules are rigid sphere and have no intermolecular attraction.

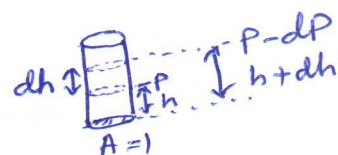
So, Sutherland improved the theory.

### Barometric distribution Law:—

Let us consider an air column of unit cross-section area over the earth surface.



Let the pr. at height  $h$  be  $P$  and at  $(h+dh)$  it is  $(P-dP)$



$$\text{change in Pr.} = P - dP - P$$

$$= -dP$$

$$= dh \rho g \quad \left[ \rho = \text{density of the gas inside the slice} \right]$$

$$\text{For ideal gas,} \quad PV = nRT = \frac{w}{M} RT \quad \left[ \begin{array}{l} w = \text{mass of the gas} \\ M = \text{Molar mass} \end{array} \right]$$

$$\Rightarrow PM = \frac{w}{V} RT = \rho RT$$

$$\Rightarrow \rho = \frac{PM}{RT}$$

$$-dP = dh \rho g = dh \cdot \frac{PM}{RT} \cdot g$$

$$\Rightarrow -\frac{dP}{P} = \frac{Mg}{RT} dh$$

$$\text{Integrating; } -\int_{P_0}^P \frac{dP}{P} = \int_0^h \frac{Mg}{RT} dh \quad \text{①}$$

$$\Rightarrow \ln \frac{P}{P_0} = - \frac{Mgh}{RT}$$

$P_0 = P_r$  at earth surface

$P = "$  " " altitude  $h$

$$\therefore P = P_0 e^{-Mgh/RT}$$

→ Barometric distribution law.

Again,  $P \propto n$   $\left[ \begin{array}{l} n = \text{no. of molecules per unit volume} \\ n_0 = " " " " " \text{at earth surface} \end{array} \right]$

$$P_0 \propto n_0$$

$$\frac{P}{P_0} = \frac{n}{n_0}; \text{ Thus, } n = n_0 e^{-Mgh/RT}$$

→ Boltzmann distribution law.

Features of Barometric Distribution law:-

- ① Pressure decreases exponentially with altitude. The exponential decrease will be more steeper for gas with higher molecular mass.



$M_2 > M_1$

- ② At a particular altitude the pressure would be more at higher temp.

Maxwell - Boltzmann distribution law:-

Maxwell distribution law of molecular speed:

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

Boltzmann distribution law:  $n = n_0 e^{-Mgh/RT} = n_0 e^{-mgh/KT}$

Replacing  $n$  in Maxwell distribution;

$$dn_c = 4\pi n_0 e^{-mgh/KT} \left( \frac{m}{2\pi KT} \right)^{3/2} c^2 e^{-mc^2/2KT} dc$$

$$= 4\pi n_0 \left( \frac{m}{2\pi KT} \right)^{3/2} c^2 e^{-(\frac{1}{2}mc^2 + mgh)/KT} dc$$

$$= 4\pi n_0 \left( \frac{m}{2\pi KT} \right)^{3/2} c^2 e^{-E/KT} dc \quad [E = KE + PE]$$

$e^{-E/KT} = \text{Boltzmann factor}$