CHAPTER 16 : STATISTICAL MECHANICS AND THERMODYNAMICS

* Statistical Mechanics:

- **Definition:**

Statistical mechanics is a branch of physics that uses statistical methods to explain and predict the properties of systems composed of a large number of particles.

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

- **Fundamental Concept:**

It focuses on microscopic behaviour of particles (atoms and molecules) to derive macroscopic properties (like temperature and pressure).

- **Relation with thermodynamics:**

Thermodynamics deal with macroscopic properties and laws governing energy exchange while statistical mechanics provides a microscopic explanation for these laws. Statistical mechanics is like calculation of thermodynamics.

SOCHBADLO BY MAK

CamScanner

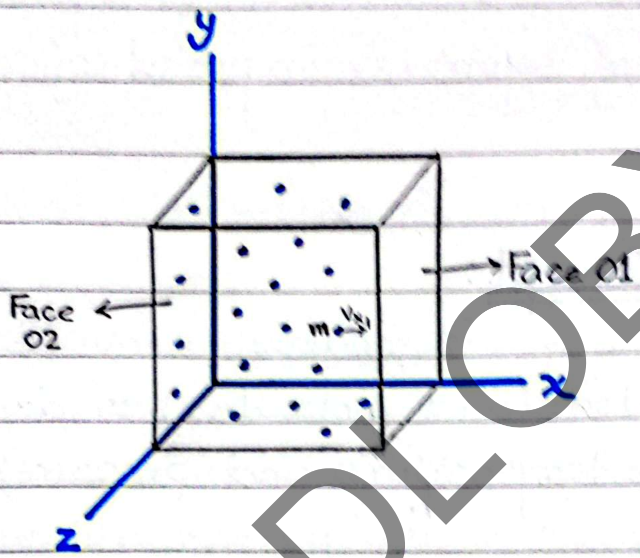
* Pressure Exerted By Gas Molecules :-

• Introduction:

The molecules of a gas are in continuous random motion in a container. They collide with one another and also with the walls of the container.

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

• Figure:



SOCHBADLOBYMAK

• Derivation:-

∴ Pressure:

$$P = \frac{F}{A} \quad \because F = \frac{\Delta \vec{P}}{\Delta t}$$

$$P = F \times \frac{1}{A}$$

$$\boxed{P = \left(\frac{\Delta \vec{P}}{\Delta t}\right) \cdot \frac{1}{A}} \longrightarrow (i)$$

∴ Change in Momentum:

Let the momentum (initial and final) of a particle of mass m and speed v_x be:

$$P_i = mv_{x_1} \quad \text{and} \quad P_f = -mv_{x_1}$$

So, change in momentum $= P_f - P_i$

$$\Delta P = -mv_{x_1} - (mv_{x_1})$$

$$= -mv_{x_1} - mv_{x_1}$$

$$\boxed{\Delta P = -2mv_{x_1}} \rightarrow \text{(ii)}$$

$\bullet \underset{-mv_{x_1}}{\overset{mv_{x_1}}{\rightleftarrows}}$

: Time taken:

$$S = vt$$

$\bullet \underset{l}{\overset{l}{\rightleftarrows}}$

$$\Delta t = \frac{S}{V}$$

$$\boxed{\Delta t = \frac{2l}{v_{x_1}}} \rightarrow \text{(iii)}$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

: Force:

$$F = \frac{\Delta P}{\Delta t}$$

$$\Rightarrow F_{x_1} = -\frac{\Delta P}{\Delta t}$$

Because this the force applied on the particle by the wall and is opposite and equal to force applied by the particle, hence it is negative.

Putting eq (ii) and (iii) in (i),

$$F_{x_1} = \frac{-(-2mv_{x_1})}{\left(\frac{2l}{v_{x_1}}\right)}$$

$$F_{x_1} = 2mv_{x_1} \div \frac{2l}{v_{x_1}}$$

$$F_{x_1} = \cancel{2}mv_{x_1} \times \frac{v_{x_1}}{\cancel{2}l}$$

$$\boxed{F_{x_1} = \frac{mv_{x_1}^2}{l}} \rightarrow \text{(1st particle)}$$

SOCHBADLOBYMAK

CS CamScanner

$$\boxed{F_{x_2} = \frac{m v_{x_2}^2}{l}} \rightarrow (2^{nd}\ \text{particle})$$

$$\boxed{F_{x_3} = \frac{m v_{x_3}^2}{l}} \rightarrow (3^{rd}\ \text{particle})$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

$$\vdots \qquad \vdots$$

$$\boxed{F_{x_n} = \frac{m v_{x_n}^2}{l}} \rightarrow (\text{nth particle})$$

Now calculating total force along x-axis,

$$F_x = F_{x_1} + F_{x_2} + F_{x_3} + \cdots + F_{x_n}$$

$$F_x = \frac{m v_{x_1}^2}{l} + \frac{m v_{x_2}^2}{l} + \frac{m v_{x_3}^2}{l} + \cdots + \frac{m v_{x_n}^2}{l}$$

$$F_x = \frac{m}{l}\left[v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \cdots + v_{x_n}^2\right]$$

Multiplying and Dividing N with above eq to get average speed,

$$F_x = \frac{mN}{l}\left[\frac{v_{x_1}^2 + v_{x_2}^2 + v_{x_3}^2 + \cdots + v_{x_n}^2}{N}\right]$$

$$F_x = \frac{mN}{l}\langle v_x^2 \rangle \quad \text{where } N = \text{Total number of particles}$$

$$\boxed{F_x = N\left[\frac{m}{l}\langle v_x^2\rangle\right]} \rightarrow (iv)$$

Here, $\langle v_x^2 \rangle$ is the mean square velocity of the gas molecules moving along x-axis.

$$\Rightarrow \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$$

Here, $\langle v^2 \rangle$ is the total mean square velocity along three dimensions (x, y, z).

SOCHBADLOBYMAK

CamScanner

Since, $\langle V_x^2 \rangle = \langle V_y^2 \rangle = \langle V_z^2 \rangle$

$$\Rightarrow \langle V^2 \rangle = \langle V_x^2 \rangle + \langle V_x^2 \rangle + \langle V_x^2 \rangle$$

$$\Rightarrow \langle V^2 \rangle = 3\langle V_x^2 \rangle$$

$$\Rightarrow \frac{\langle V^2 \rangle}{3} = \langle V_x^2 \rangle$$

$$\Rightarrow \boxed{\langle V_x^2 \rangle = \frac{\langle V^2 \rangle}{3}} \rightarrow (v)$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

Putting eq (v) in (iv), then

$$F_x = \frac{Nm}{\ell}\left[\frac{\langle V^2 \rangle}{3}\right]$$

Hence, total force is given by:

$$\Rightarrow \boxed{F = \frac{Nm}{\ell}\left[\frac{\langle V^2 \rangle}{3}\right]} \rightarrow (vi)$$

$\because$ Pressure $= \frac{\text{Force}}{\text{Area}}$

$$P = \frac{F}{A} \qquad \because \text{Area} = \ell \times \ell = \ell^2$$

Now, putting the values of force and area, then

$$P = \frac{Nm}{\ell}\left[\frac{\langle V^2 \rangle}{3}\right] \div (\ell^2)$$

$$P = \frac{Nm}{\ell}\left[\frac{\langle V^2 \rangle}{3}\right] \times \frac{1}{\ell^2}$$

$$P = \frac{Nm}{3\ell^3}\left[\langle V^2 \rangle\right]$$

SOCHBADLOBYMAK

CamScanner

Since, volume = $l \times l \times l$

$$\boxed{V = l^3}$$

$$\boxed{P = \frac{Nm}{3V}\langle v^2 \rangle}$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

Relation between pressure and Average Translational Kinetic Energy:

Since, $P = \frac{mN}{3V}\langle v^2 \rangle$ $\qquad \langle K.E \rangle = \frac{1}{2} m \langle v^2 \rangle$

Multiplying and dividing 2,

$$P = \frac{mN}{3V}\langle v^2 \rangle \times \frac{2}{2}$$

$$P = \frac{2N}{3V} \times \frac{1 m \langle v^2 \rangle}{2}$$

$$P = \frac{2N}{3V} \times [\langle K.E \rangle] \Rightarrow P = \frac{2}{3} N_o [\langle K.E \rangle]$$

$\frac{N}{V} = N_o$ No of molecules per unit volume.

$\because \frac{2}{3}N_o$ or $\frac{2N}{3V}$ = constant (Bcz the number of molecules and volume of box do not change)

$$P = \text{constant} \times \langle K.E \rangle$$

$$P \propto \langle K.E \rangle$$

- **Relation of Pressure with Density:**

$$P = \frac{Nm}{3V}\langle v^2 \rangle \qquad \rho = \frac{m}{V}$$

SOCHBADLOBYMAK

CamScanner

If there are N molecules in the container, then density becomes,

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

So, $P = \frac{1}{3} \times \left(\frac{Nm}{V}\right) \times \langle v^2 \rangle$

$$\boxed{P = \frac{1}{3}\rho\langle v^2\rangle}$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

- **Temperature in terms of average translational kinetic energy of gas molecules:**

Since, $\boxed{PV = nRT} \rightarrow (i)$

Since, Number of moles = $\frac{\text{No of molecules}}{\text{Avagadro's number}}$

$$\boxed{n = \frac{N}{N_A}} \rightarrow (ii)$$

Putting eq (ii) in eq (i),

$$PV = \frac{N}{N_A} \times R \times T \qquad \because R = \text{Universal gas constant}$$

$$PV = N \times \frac{R}{N_A} \times T \qquad \because \frac{R}{N_A} = k \text{ (Boltzmann constant)}$$

$$\boxed{PV = NkT} \rightarrow (iii)$$

Since, we have:-

$$P = \frac{2N}{3V} \times \frac{1}{2} m\langle v^2\rangle$$

$$\boxed{PV = \frac{2N}{3} \times \frac{1}{2} m\langle v^2\rangle} \rightarrow (iv)$$

SOCHBADLOBYMAK

CamScanner

By comparing eq (iii) and (iv),

$$\cancel{N}kT = \frac{2\cancel{N}}{3} \times \frac{1}{2}m\langle v^2 \rangle$$

$$T = \frac{2}{3k} \times \frac{1}{2}m\langle v^2 \rangle \qquad \because \langle K.E \rangle = \frac{1}{2}m\langle v^2 \rangle$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

$$T = \frac{2}{3k} \times \langle K.E \rangle$$

Since, $\frac{2}{3k}$ is constant,

$$T = \text{constant} (\langle K.E \rangle)$$

$$\boxed{T \propto \langle K.E \rangle}$$

Q1. Why force is taken negative?

Ans Force is taken negative because it was acting in opposite direction, like action and reaction, first force was applied by the molecule on the wall and the force written in the derivation is applied on the molecule by the wall.

Q2. Why the final momentum is taken negative?

Ans Momentum of a particle is positive if it moves along +ve x-axis towards the wall and it is negative if it moves in -ve x-axis after striking the wall. When we take its change, momentum results in being negative.

Q3. What is the reason for writing $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$?

Ans If we want to find the total velocity, we need

SOCHBADLOBYMAK

CS CamScanner

to add the velocities along x-axis, y-axis and z-axis. That is why, we have written that total average velocity $\langle v^2 \rangle$ is equal to $\langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$.

Q4. Why $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$?

Ans The velocities along x, y and z axes are same because the gas is in a small container. Since, no external changes (external force or energy) are affecting the gas the motion is uniformly distributed in all directions/ dimensions.

* Root Mean Square Speed of Gas Molecules:

- **Definition:**

The square root of the mean square speed of the gas molecules is called root mean square (rms) speed of the molecules.

- **Derivation:**

If there are a number of velocities $v_1, v_2, v_3, \ldots v_n$, their net square would be

$$\langle v^2 \rangle = v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2$$

⇒ **Mean Square:**

$$\langle v^2 \rangle = \frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2}{N}$$

⇒ **Square Root:**

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \cdots + v_n^2}{N}}$$

SOCHBADLOBYMAK

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

CamScanner

$\Rightarrow$ RMS :

$$\boxed{V_{r.m.s} = \sqrt{\frac{v_1^2+v_2^2+v_3^2+\cdots+v_n^2}{N}}} \rightarrow (i)$$

• **Relation of $V_{r.m.s}$ with temperature:**

Since the pressure of gas molecules is:

$$P = \frac{1}{3}\frac{mN}{V}\langle v^2\rangle$$

$$\boxed{PV = \frac{1}{3}mN\langle v^2\rangle} \rightarrow (i)$$

Since, from ideal gas equation,

$$PV = nRT \qquad \because n = \frac{N}{N_A}$$

$$PV = \frac{N}{N_A}RT$$

$$PV = N\left(\frac{R}{N_A}\right)T \qquad \because \frac{R}{N_A} = K$$

$$\boxed{PV = NkT} \rightarrow (ii)$$

Comparing (i) and (ii),

$$\cancel{N}kT = \frac{1}{3}m\cancel{N}\langle v^2\rangle$$

$$\frac{3kT}{m} = \langle v^2\rangle$$

or $\langle v^2\rangle = \frac{3kT}{m}$

Taking square root on both sides,

$$\sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}}$$

$$V_{r.m.s} = \sqrt{\frac{3k}{m}}\cdot\sqrt{T}$$

SOCHBADLOBYMAK

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

CS CamScanner

$\because \sqrt{\frac{3k}{m}} = \text{constant}$

$\Rightarrow V_{r.m.s} = \text{Constant} \times \sqrt{T}$

$$\boxed{V_{r.m.s} \propto \sqrt{T}}$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

This relation tells that if the value of temperature increases then, the value of $V_{r.m.s}$ also increases.

- **Relation of $V_{r.m.s}$ with Molar Mass (M):**

Since,

$$\boxed{V_{r.m.s} = \sqrt{\frac{3kT}{m}}} \rightarrow (i)$$

$\because k = \frac{R}{N_A}$

$$V_{r.m.s} = \sqrt{\frac{3T}{m} \times k}$$

$$V_{r.m.s} = \sqrt{\frac{3T}{m} \times \frac{R}{N_A}}$$

$$\boxed{V_{r.m.s} = \sqrt{\frac{3TR}{mN_A}}} \rightarrow (ii)$$

Since, mN_A → Avagadro's no

↓ mass of single molecule

$$\Rightarrow \boxed{mN_A = M} \rightarrow (iii)$$

Putting eq (iii) in (ii),

$$V_{r.m.s} = \sqrt{\frac{3TR}{M}} \Rightarrow V_{r.m.s} = \sqrt{3TR} \times \frac{1}{\sqrt{M}}$$

SOCHBADLOBYMAK

CamScanner

$$V_{r.m.s} = (\text{constant}) \times \frac{1}{\sqrt{M}} \Rightarrow \boxed{V_{r.m.s} \propto \frac{1}{\sqrt{M}}}$$

- **Relation of $V_{r.m.s}$ with Pressure (P) :-**

Since we have,

$$\Rightarrow P = \frac{1}{3} \rho \langle v^2 \rangle$$

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

$$3P = \rho \langle v^2 \rangle$$

$$\frac{3P}{\rho} = \langle v^2 \rangle$$

$$\langle v^2 \rangle = \frac{3P}{\rho}$$

Taking square root on both sides,

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3P}{\rho}} \Rightarrow \boxed{V_{r.m.s} = \sqrt{\frac{3P}{\rho}}}$$

Q5. What RMS stands for?

Ans RMS stands for Root Mean Square.

S :- Squaring both values of velocity given for one molecule to get positive velocity.

M :- Mean or average taken because squared value (lets say 9) is out of original value (lets say 3). So mean value is 4.5.

R :- Square Root is taken to get the value under range of the original value. So the value after square root of 4.5 is 2.12 that is lesser than 3.

So, $2.12\ ms^{-1}$ is effective velocity or $V_{r.m.s}$.

SOCHBADLOBYMAK

CamScanner

Q6. Why we calculate the effective velocity/ $v_{r.m.s}$?

Ans If we have a container with molecules whose velocity keeps changing. Firstly, the particles move in x-axis direction. After bouncing from the wall of the container, it starts moving towards -x-axis. So, the velocity is not constant and keeps on changing, so we need a value that represents this motion in a steady way. So, we calculate $v_{r.m.s}$ which gives us a constant or representative effective velocity, even when the actual velocities keep changing.

Q7. What is the relation of $V_{r.m.s}$ with temperature and mass?

Ans. • The effective speed increases with temperature.

• Lighter gases move faster than heavier gases at the same temperature.

SOCHBADLOBYMAK

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

Q8. What is an ideal gas?

Ans An ideal gas is a theoretical gas model in which:-

• The intermolecular forces of attraction between gas molecules are considered to be zero.

• The volume occupied by the gas molecules themselves is considered to be negligible when compared to total volume of container.

CamScanner

Q8. Why real gases deviate from ideal behaviour?

OR

What are the limitations of ideal gas equation?

Ans Gas molecules deviate from ideal behaviour at:

→ At High Pressure:

The gas molecules are compressed by increasing pressure, as a result, they liquify. In the liquid state, they have intermolecular attractive forces and a considerable volume.

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

→ At Low Temperature:

When we lower the temperature, the speed of gas molecules slows down and the gas liquifies. As a result, they have intermolecular attractive forces between them and also attain a volume.

Q10. When real gases obey ideal behaviour?

Ans Gas molecules behave ideally at :-

→ At low pressure:

The gas molecules are not compressed and move away from each other when their pressure is decreased. So, there would be no attractive forces between the gas molecules and their volume would be negligible.

→ At high temperature:

At high temperature, the speed of gas molecules increases, so they get far away from each other. So, their volume or the attractive forces would be negligible.

SOCHBADLOBYMAK

CamScanner

Q11. Why Van der Waals theory modified ideal gas equation?

Ans The Van der Waals theory explains the behaviour of real gases by accounting for the attractive and repulsive forces between molecules. It modifies ideal gas law to include two key factors:

1) **Molecular Size:**

Real gas molecules occupy space, reducing the available volume.

2) **Intermolecular Forces:**

Attractive forces between the molecules are affected by pressure.

Equation:

The modified equation is:

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

$$\left[P + \frac{an^2}{V^2}\right]\left[V - nb\right] = nRT$$

Where a = attractive force constant, and
b = molecular size constant

Benefit/Use:

This theory helps predict real gas behaviour more accurately than the ideal gas law.

* Ideal Gas	Non-Ideal Gas
Intermolecular forces	
No intermolecular forces are present.	Intermolecular forces (attractive or repulsive) exist between particles.

SOCHBADLOBYMAK

CamScanner

Volume	
Volume of gas molecules is considered negligible.	Molecules have finite volume that affects gas behaviour.
Obedience to Gas Laws	
Perfectly obeys the ideal gas law ($PV=nRT$) under all conditions.	Deviates from the ideal gas law, especially at high pressure and low temperature.
Conditions	
Assumes ideal behaviour at low pressure and high temperature.	Shows non-ideal behaviour mainly at low temperature and high pressure.
Collision Assumptions	
Collisions between gas molecules are perfectly elastic (no energy loss).	Collision may involve energy loss due to intermolecular forces.
Examples	
Hypothetical gas is used in theory (no real gas is perfectly ideal).	Real gases like:- CO_2, NH_3, CH_4, etc.

SOCHBADLOBYMAK

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

* **Superconductivity:-**

- **Definition:**

Superconductivity is a phenomenon in which certain materials conduct electricity without ~~eoll~~ resistance when cooled below a specific critical temperature (T_c).

- **Superconductors:**

Materials whose resistivity becomes ~~low~~ zero

CS CamScanner

at very low temperatures.

• **Critical Temperature (T_c):**

It is the temperature below which resistivity of superconductors drops to zero.

• **Discovery:**

This was found in 1911 by Heike Kamerlingh Onnes in mercury at 4.2K. Later, other materials showed superconductivity at higher temperatures (e.g. 125 K).

GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353

• **Applications:**

Superconductivity is used in:-

1) Powerful electromagnets
2) Particle accelerators
3) Magnetic levitation trains (Maglev)
4) Electric motors
5) Fast computer chips
6) Efficient power transmission lines

Q12. What is resistivity? How it is linked with superconductivity?

Resistivity:-

• **Definition:**

Resistivity is a material's intrinsic property that measures its opposition to the flow of electric current.

SOCHBADLOBYMAK

CamScanner

- **Symbol:**

  It is represented by symbol ρ (rho).

- **Unit:**

  It is measured in ohmmeters (Ωm).

- **Resistivity in superconductors:**

  In a superconductor, resistivity drops to zero when the material is cooled below a specific critical temperature. This means that once a current is started, it can flow idefinitely without any energy loss.

Q12. Why resistance drops to zero in superconductors as compared to usual metals?

⇒ **Usual Metals:**

In usual metals, the electrons flow in a scattered form which cause alot of resistivity in metals.

⇒ **Superconductors:**

In superconductors, the electrons do not flow in a scattered form but ~~play~~ flow in a straight way which does not cause any resistivity. Electrons form Cooper pairs of electrons, which move without scattering.

SOCHBADLOBYMAK
GET ADMISSION IN OUR ONLINE INSTITUTE
SOCH BADLO BY MAK
Contact WhatsApp Number: +92 331 5014353
CamScanner