Digital Classes for B. Sc. Physics

Kinetic Theory of Gases

(NEP Semester IV - Chapter 3)

Dr. DEBOJYOTI HALDER
Department of Physics,
R. B. C. Evening College

Ideal Gas Equation

Boyle's Law

states :

"The pressure of a fixed mass of gas at constant temperature is inversely proportional to its volume."

OR

$$P \propto \frac{1}{V} \quad \text{if} \quad T = \text{constant}$$

- The related equations to the Boyle's law are

$$PV = \text{constant}$$

OR

$$P_1V_1 = P_2V_2$$

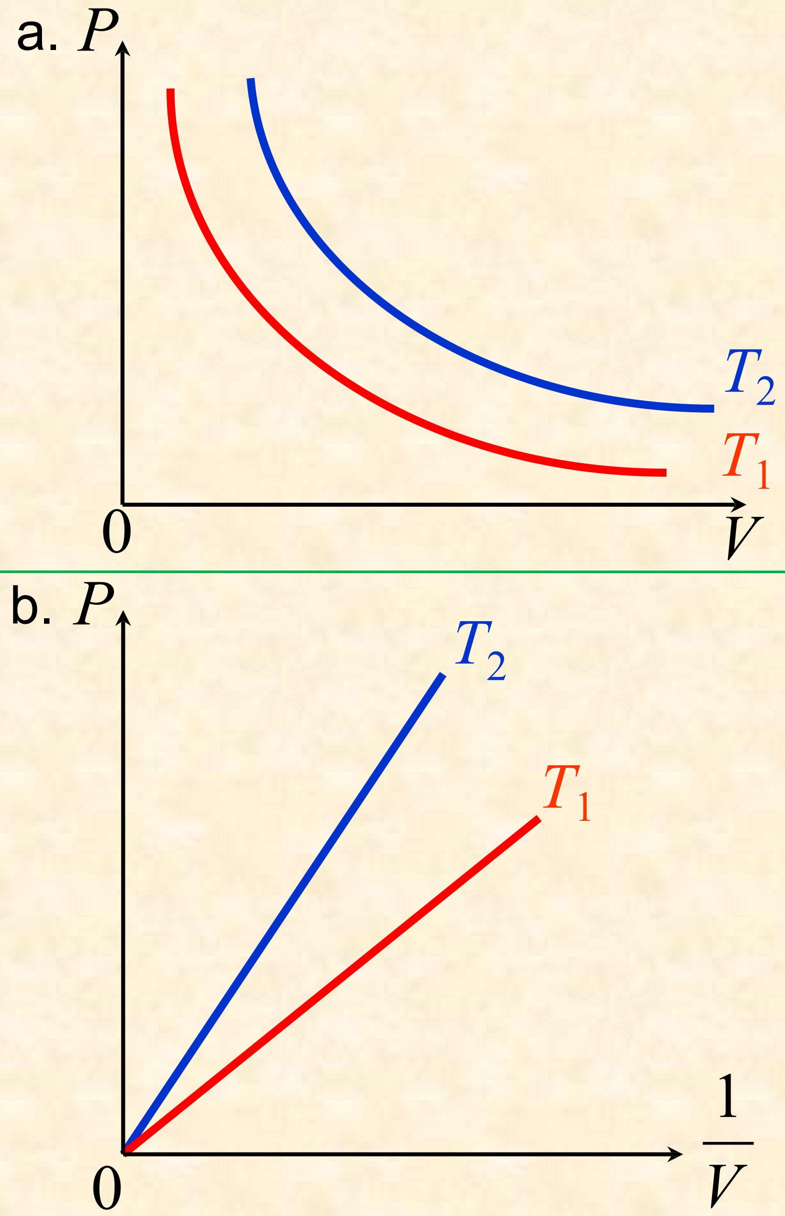
where P_1 : initial pressure

P_2 : final pressure

V_1 : initial volume

V_2 : final volume

- **Graphs of the Boyle's law.**



The pressure of a fixed mass of gass at constant temperature is inversely proportional to its volume.

Charles's law

- states:

"The volume of a fixed mass of gas at constant pressure is directly proportional to its absolute temperature."

OR

$$V \propto T \quad \text{If} \quad P = \text{constant}$$

The related equations to the Charles' law are

$$\frac{V}{T} = \text{constant}$$

OR

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

where

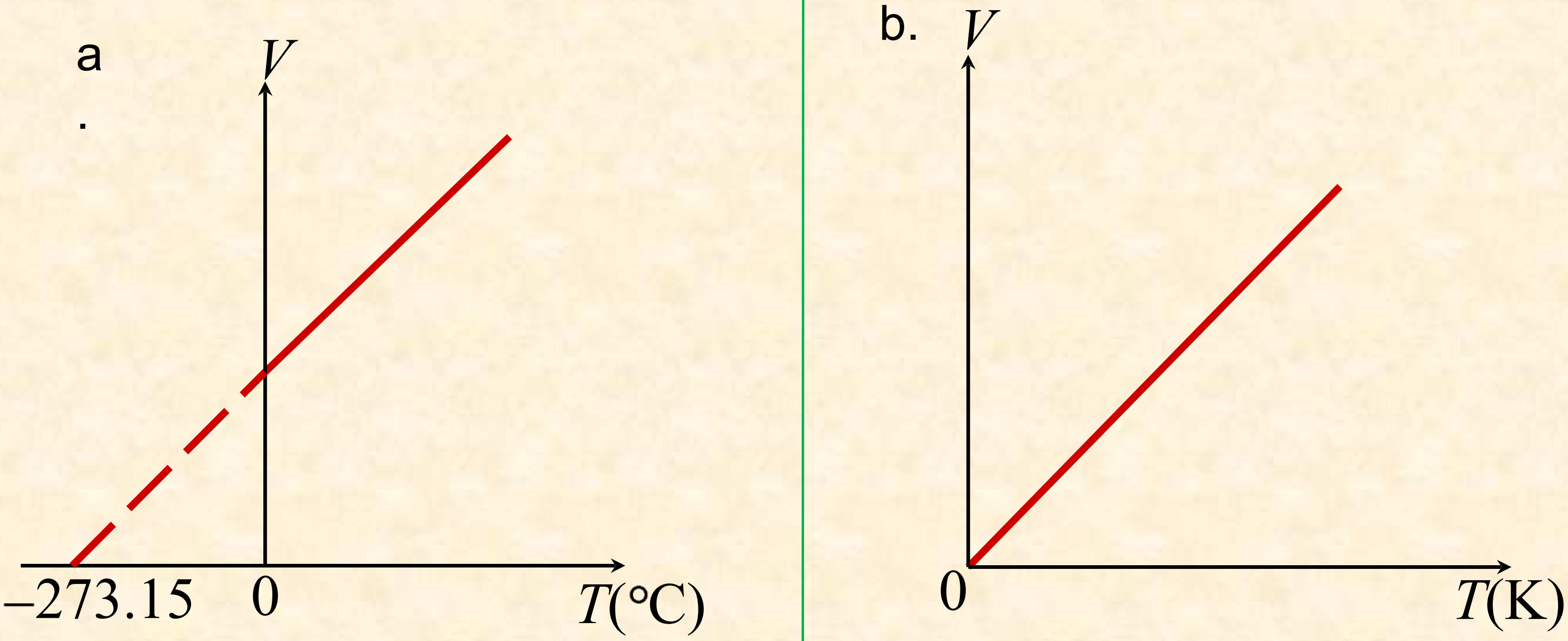
T_1 : initial absolute temperature

T_2 : final absolute temperature

V_1 : initial volume

V_2 : final volume

Graphs of the Charles's law.



Gay-Lussac's (pressure) law

states :

"The pressure of a fixed mass of gas at constant volume is directly proportional to its absolute temperature."

OR

$$P \propto T \text{ If } V = \text{constant}$$

The related equations to the Gay-lussac's law are

$$\frac{P}{T} = \text{constant}$$

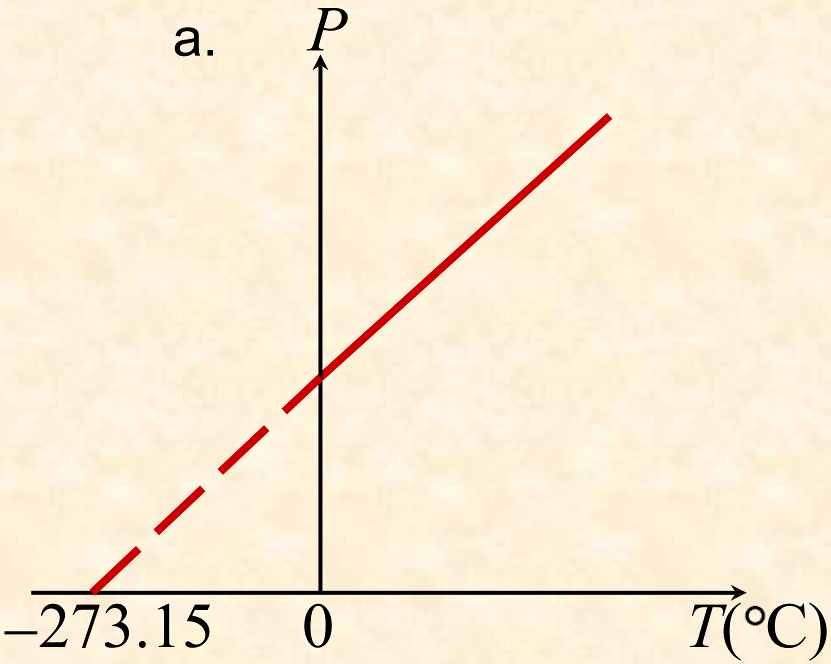
OR

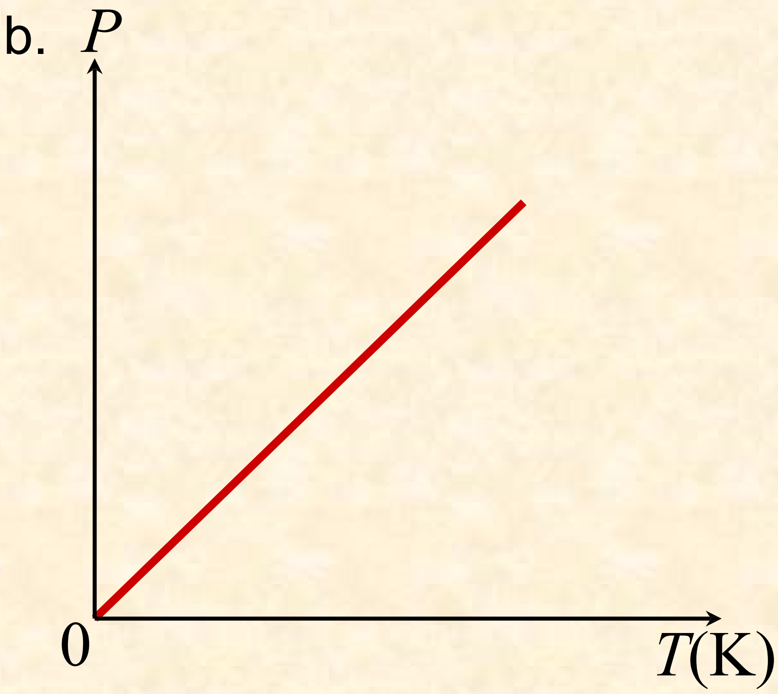
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

where

T_1 : initial absolute temperature
T_2 : final absolute temperature
P_1 : initial pressure
P_2 : final pressure

Graphs of the Gay-lussac’s (pressure) law





Equation of state for an ideal gas

- An **ideal gas** is defined as **a perfect gas which obeys the three gas laws (Boyle's, Charles's and Gay-Lussac's) exactly**.
- Consider an ideal gas in a container changes its pressure P, volume V and temperature T as shown in Figure 1.

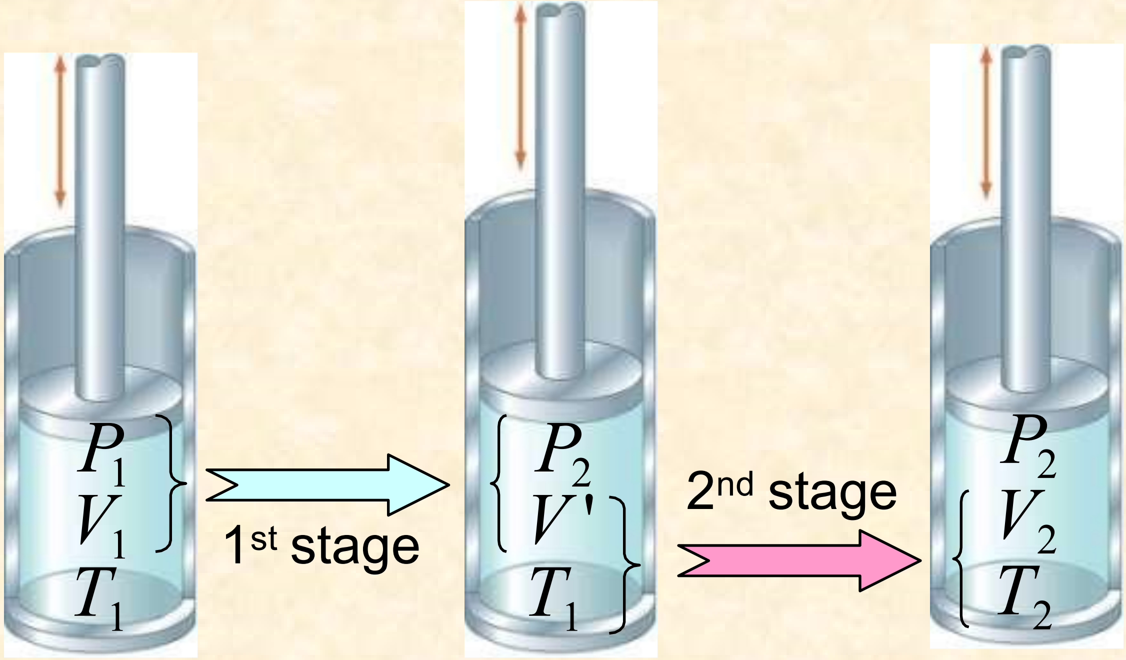


Figure 1

- In 1st stage, temperature is kept at T_1 ,
  Using Boyle's law :

$$P_2 V' = P_1 V_1$$

$$\Rightarrow \quad V' = \frac{P_1 V_1}{P_2} \qquad \text{———}(1)$$

- In 2nd stage, pressure is kept constant at P_2 ,
  Using Charles's law :

$$\frac{V'}{T_1} = \frac{V_2}{T_2}$$

$$\Rightarrow \quad V' = \frac{V_2 T_1}{T_2} \qquad \text{———} \quad (2)$$

- Equating eqs. (1) and (2), thus

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Initial

Final

OR

$$\frac{PV}{T} = \text{constant} \qquad \text{———} \qquad (3)$$

- Consider **1 mole** of gas at **standard temperature and pressure (S.T.P.)**, T = **273.15 K**, P = **101.3 kPa** and V_m = **0.0224 m³**
  - From equation (3),

$$R = \frac{PV_\mathrm{m}}{T} = \frac{(101.3\times10^3)(0.0224)}{273.15}$$

$$R = 8.31\ \mathrm{J\ K^{-1}\,mol^{-1}}$$

where ***R*** is called **molar gas constant** and its **value** is the **same for all gases**.

  - Thus $$\frac{PV_\mathrm{m}}{T} = R$$

$$PV_\mathrm{m} = RT$$ where V_m : volume of 1mole gas

- For ***n* mole** of an **ideal gas**, **the equation of state** is written as

$$\boxed{PV = nRT}$$

  - where n : the number of mole gas

$$\boxed{n = \frac{m}{M}}$$

where

m : mass of a gas

M : molar mass of a gas

OR

$$\boxed{n = \frac{N}{N_{\mathrm{A}}}}$$

where

N : number of molecules

N_{A} : Avogadro's constant

$= 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$

– If the Boltzmann constant, k is defined as

$$\boxed{k = \frac{R}{N_{\mathrm{A}}} = 1.38 \times 10^{-23}\ \mathrm{J\ K}^{-1}}$$

then the equation of state becomes

$$\boxed{PV = NkT}$$

Example 1 :

The volume of vessel A is three times of the volume vessel B. The vessels are filled with an ideal gas and are at a steady state. The temperature of vessel A and vessel B are at 300 K and 500 K respectively as shown in Figure 2.

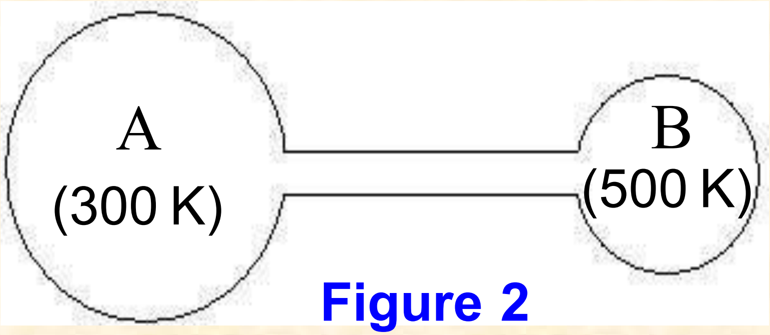


Figure 2

If the mass of the gas in the vessel A is m, obtain the mass of the gas in the vessel B in terms of m.

Solution :

$$V_A = 3V_B; m_A = m; T_{0A} = 300\,\text{K}; T_{0B} = 500\,\text{K}$$

Since the vessels A and B are connected by a narrow tube thus the pressure for both vessels is same, finally i.e.

$$P_A = P_B = P$$

The system is in the steady state, thus

$$T_{0A} = T_A = 300\,\text{K}; T_{0B} = T_B = 500\,\text{K}$$

By applying the equation of state for an ideal gas,

$$PV = nRT \text{ and } n = \frac{m}{M}$$

$$PV = \left(\frac{m}{M}\right)RT$$

Therefore,

Vessel A :

$$P_A V_A = \left(\frac{m_A}{M}\right) R T_A$$

$$P\,3V_B = \left(\frac{m}{M}\right) R\,300$$

Vessel B :

$$V_A = 3V_B;\ m_A = m;\ T_{0A} = 300\,\mathrm{K};\ T_{0B} = 500\,\mathrm{K}$$

$$PV_B = 100\left(\frac{m}{M}\right)R \tag{1}$$

$$PV_B = 500\left(\frac{m_B}{M}\right)R \tag{2}$$

By equating the eqs. (1) and (2) hence

$$100\left(\frac{m}{M}\right)R = 500\left(\frac{m_B}{M}\right)R$$

$$m_B = \frac{m}{5}$$

2. Kinetic theory of gases

- The macroscopic behaviour of an ideal gas can be describe by using the equation of state but the **microscopic behaviour** only can be describe by **kinetic theory of gases.**

1 Assumption of kinetic theory of gases

- All gases are made up of **identical atoms or molecules.**
- All atoms or molecules move **randomly and haphazardly**.
- The **volume** of the atoms or molecules is **negligible** when **compared** with the **volume occupied by the gas.**
- The **intermolecular forces** are **negligible except during collisions.**
- Inter-atomic or molecular **collisions** are **elastic.**
- The **duration of a collision** is **negligible compared** with the **time spent travelling between collisions.**
- Atoms and molecules move with **constant speed between collisions. Gravity has no effect** on molecular motion.

2 Force exerted by an ideal gas

- Consider an ideal gas of N molecules are contained in a cubical container of side d as shown in Figure 4.

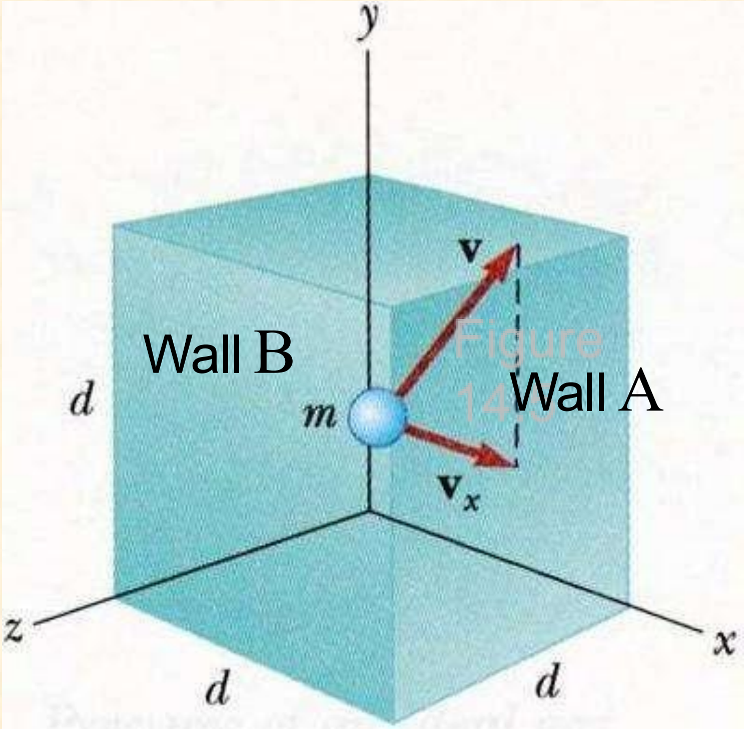


Figure 4

- Let each molecule of the gas have the mass m and velocity v.
- The velocity, v of each molecule can be resolved into their components i.e. v_x, v_y and v_z.
- Consider, initially a single molecule moving with a velocity v_x towards wall A and after colliding elastically , it moves in the opposite direction with a velocity $-v_x$ as shown in Figure 5.

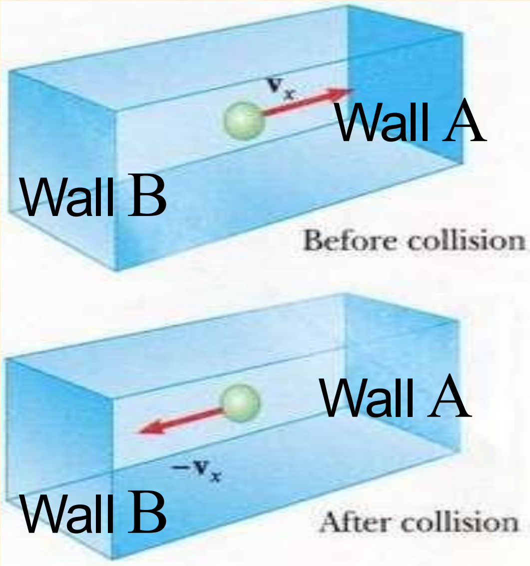


Figure 5

Therefore the change in the linear momentum of the molecule is given by

$$\Delta P_x = -mv_x - (mv_x)$$

$$\Delta P_x = -2mv_x$$

The molecule has to travel a distance 2d (from A to B and back to A) before its next collision with wall A. The time taken for this movement is

$$\Delta t = \frac{2d}{v_x}$$

If F_{x1} is the magnitude of the average force exerted by a molecule on the wall in the time Δt, thus by applying Newton's second law of motion gives

$$F_{x1} = \frac{\Delta P_x}{\Delta t} = \frac{2mv_x}{\left(\frac{2d}{v_x}\right)} \Rightarrow F_{x1} = \left(\frac{m}{d}\right) v_x^{\,2}$$

For N molecules of the ideal gas,

$$F_x = \left(\frac{m}{d}\right) v_{x1}^{\,2} + \left(\frac{m}{d}\right) v_{x2}^{\,2} + \ldots\ldots + \left(\frac{m}{d}\right) v_{xN}^{\,2}$$

$$F_x = \frac{m}{d}\left(v_{x1}^{\,2} + v_{x2}^{\,2} + \ldots\ldots + v_{xN}^{\,2}\right)$$

where v_{x1} is the x of x component of velocity of molecule 1, v_{x2} is the component of velocity molecule 2 and so on.

- The mean (average) value of the square of the velocity in the x direction for N molecules is

$$< v_x^{\;2} >= \frac{v_{x1}^{\;2} + v_{x2}^{\;2} + \ldots\ldots + v_{xN}^{\;2}}{N}$$

$$v_{x1}^{\;2} + v_{x2}^{\;2} + \ldots\ldots + v_{xN}^{\;2}$$
$$= N < v_x^{\;2} >$$

Thus, the x component for the total force exerted on the wall of the cubical container is

$$F_x = \frac{m}{d} N < v_x^{\;2} >$$

- The magnitude of the velocity v is given by

$$v^2 = v_x^{\;2} + v_y^{\;2} + v_z^{\;2}$$

then

$$< v^2 >=< v_x^{\;2} > + < v_y^{\;2} > + < v_z^{\;2} >$$

- Since the velocities of the molecules in the ideal gas are **completely random**, there is **no preference to one direction or another**. Hence $$< v_x^2 > = < v_y^2 > = < v_z^2 >$$
$$< v^2 > = 3 < v_x^2 >$$
$$< v_x^2 > = \frac{< v^2 >}{3}$$

- The total force exerted on the wall in all direction, F is given by

$$F = \frac{m}{d} N < v_x^2 > \Rightarrow F = \frac{m}{d} N \left(\frac{< v^2 >}{3} \right)$$

$$F = \frac{N}{3} \left(\frac{m < v^2 >}{d} \right)$$

where $< v^2 >$: mean square velocity of the molecule

3 Pressure of an ideal gas

- From the definition of pressure,

$$P = \frac{F}{A}$$ where $$A = d^2$$ and $$F = \frac{N}{3}\left(\frac{m < v^2 >}{d}\right)$$

$$P = \frac{1}{3}\left(\frac{Nm < v^2 >}{d^3}\right)$$ and $$d^3 = V$$

$$P = \frac{1}{3}\left(\frac{Nm}{V} < v^2 >\right) \quad \text{-----------------------------(1)}$$

$$PV = \frac{1}{3}\left(Nm < v^2 >\right) \quad \text{-----------------------------(2)}$$

where Nm : mass of an ideal gas in the container

- Since the density of the gas, ρ is given by

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

hence the equation (15.1) can be written as

$$P = \frac{1}{3}\rho < v^2 > \qquad \text{——— (3)}$$

where

P : pressure by the gas

ρ : density of the gas

$< v^2 >$: mean square velocity of the gas molecules

4 Root mean square velocity (v_{rms})

- is defined as $v_{\mathrm{rms}} = \sqrt{< v^2 >}$

- From the equation of state in terms of Boltzmann constant, k :

$$PV = NkT \qquad \text{------------------ (4)}$$

- By equating the eqs. (15.4) and (14.2), thus

$$NkT = \frac{1}{3}Nm < v^2 >$$

$$< v^2 > = \frac{3kT}{m}$$

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

OR

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

where

v_{rms}: root mean square velocity (speed)

m: mass of a molecule gas

M: molar mass of a gas

T: absolute temperature

- Since

$$P = \frac{1}{3}\rho < v^2 >$$

thus

$$< v^2 > = \frac{3P}{\rho}$$

therefore the equation of root mean square velocity of the gas molecules also can be written as

$$v_{rms} = \sqrt{\frac{3P}{\rho}}$$

Molecular kinetic energy and internal energy

1. Translational kinetic energy of molecule

- From equation (1), thus

$$P = \frac{1}{3}\left(\frac{Nm}{V} < v^2 >\right)$$

$$P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2} m < v^2 >\right) \qquad \text{.................................(5)}$$

This equation shows that

P increases (↑) When

$\left(\frac{N}{V}\right)$ increases

$\left(\frac{1}{2} m < v^2 >\right)$ increases

1 Translational kinetic energy of molecule

This equation shows that

P increases (↑) When

$\left(\dfrac{N}{V}\right)$ increases

$\left(\dfrac{1}{2}m<v^2>\right)$ increases

Rearrange equation (14.5), thus

$$PV=\frac{2}{3}N\left(\frac{1}{2}m<v^2>\right)$$

and

$$PV=NkT$$

$$NkT = \frac{2}{3}N\left(\frac{1}{2}m < v^2 >\right)$$

$$\frac{1}{2}m < v^2 >= \frac{3}{2}kT$$

and

$$\frac{1}{2}m < v^2 >= K_{\mathrm{tr}}$$

$$K_{\mathrm{tr}} = \frac{3}{2}kT = \frac{3}{2}\left(\frac{R}{N_{\mathrm{A}}}\right)T$$

where

K_{tr} : average translational kinetic energy of a molecule

T : absolute temperature

k : Boltzmann constant

R : molar gas constant

N_{A} : Avogadro constant

- For N molecules of an ideal gas in the cubical container, the total average (mean) translational kinetic energy, E is given by

$$E = NK_{tr}$$

$$E = N\left(\frac{3}{2}kT\right)$$

$$E = \frac{3}{2}NkT$$

OR

$$E = \frac{3}{2}nRT$$

2 Principle of equipartition of energy

- States : "**the mean (average) kinetic energy of every degrees of freedom of a molecule is** $\frac{1}{2}kT.$

Therefore

$$< K >= \frac{f}{2}kT$$

→ Mean (average) kinetic energy per molecule

OR

$$< K >= \frac{f}{2}RT$$

→ Mean (average) kinetic energy per mole

where f : degrees of freedom

T : absolute temperature

3 Degree of freedom (f)

is defined as a **number of independent ways in which an atom or molecule can absorb or release or store the energy**.

Monatomic gas (e.g. He,Ne,Ar)

- The number of degrees of freedom is **3** i.e. **three direction of translational motion** where contribute translational kinetic energy as shown in Figure 6.

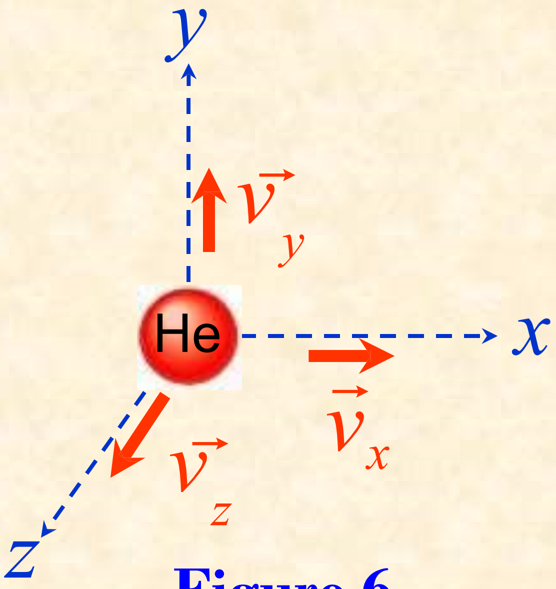


Figure 6

Diatomic gas (e.g. H_2, O_2, N_2)

- The number of degrees of freedom is

Translational kinetic energy → 3

Rotational kinetic energy → 2

5

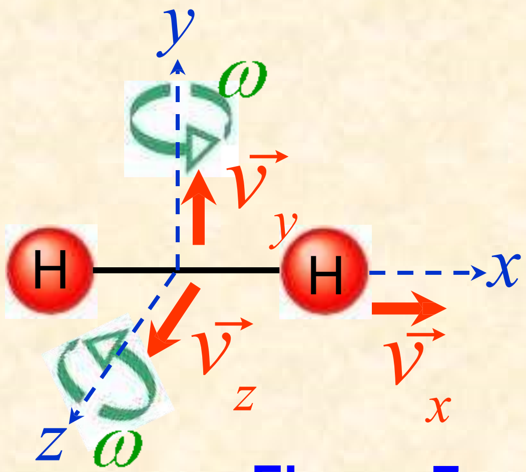


Figure 7

Polyatomic gas (e.g. H_2O, CO_2, NH_3)

- The number of degrees of freedom is

Translational kinetic energy → 3

Rotational kinetic energy → 3

6

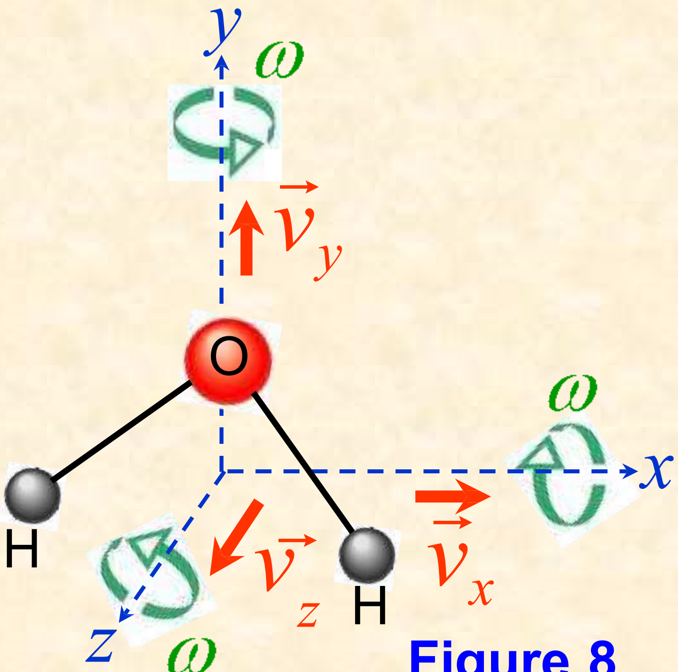


Figure 8

Table 1 shows the degrees of freedom for various molecules

Molecule	Example	Degrees of Freedom (f)			Average kinetic energy per molecule, $<K>$
		Translational	Rotational	Total	
Monatomic	He	3	0	3	$\frac{3}{2}kT$
Diatomic	H_2	3	2	5	$\frac{5}{2}kT$
Polyatomic	H_2O	3	3	6	$\frac{6}{2}kT = 3kT$

(At temperature of 300 K)

- Degrees of freedom depend on the **absolute temperature of the gases**.
  - For example : Diatomic gas (H_2)
  - Hydrogen gas have the vibrational kinetic energy (as shown in Figure 9) where contribute **2 degrees of freedom** which correspond to the **kinetic energy and the potential energy associated with vibrations along the bond** between the atoms.

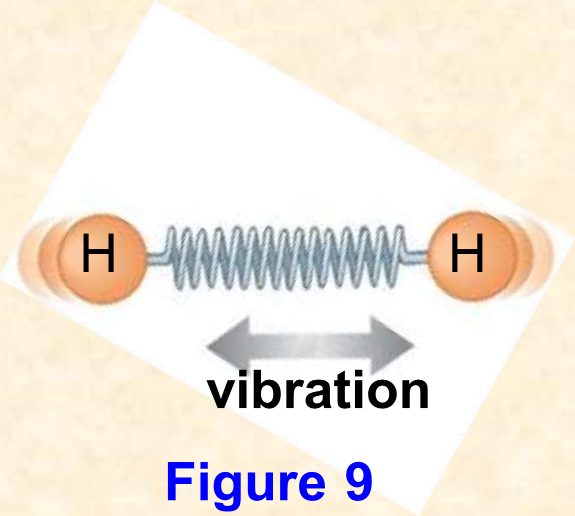


Figure 9

when the temperature,

At **250 K** ⇨ $f = 3$

At **250 – 750 K** ⇨ $f = 5$

At **>750 K** ⇨ $f = 7$

4 Internal energy of gas and relate the internal energy to the number of degree of freedom

- is defined as the **sum of total kinetic energy and total potential energy of the gas molecules**.

- But in ideal gas, the intermolecular forces are assumed to be negligible thus the **potential energy** of the molecules can be **neglected**.

Thus for N molecules,

$$U = N < K >$$

$$U = \frac{f}{2} NkT$$ and $$k = \frac{R}{N_A}$$

OR

$$U = \frac{f}{2} nRT$$

where U : internal energy of the gas

Table 2 shows the properties for 1 mole of an ideal gas

	Monatomic	Diatomic	Polyatomic
Degrees of freedom, f	3	5	6
Average kinetic energy per molecule, $\langle K \rangle$	$\frac{3}{2}kT$	$\frac{5}{2}kT$	$\frac{6}{2}kT = 3kT$
Internal energy, U	$\frac{3}{2}RT$	$\frac{5}{2}RT$	$\frac{6}{2}RT = 3RT$