B.Sc. (Honours) Part-I
Paper-IA

Topic: Gaseous State-Kinetic Gas Theory and Gas Law

UG
Subject-Chemistry

Dr. Laxman Singh
Asst. Professor
Department of Chemistry
R.R.S. College (PPU)
(Mokama, Patna)
Email:laxmanrsearcher84@gmail.com

States of Matter

4.1 INTRODUCTION

Matter is capable of existing in three physical states: solid, liquid and gas. Matter is anything which has mass and occupies space. Any substance can exist in either of three states depending on temperature and pressure. Liquid and solid states are condensed states as they have much higher densities. Both liquids and gases are termed as fluids as they have flowing ability.

The three states of a substance are interconvertible by variation of temperature and pressure. A liquid state is intermediate between the gaseous state (complete molecular randomness) and the solid state (orderly arrangement of molecules).

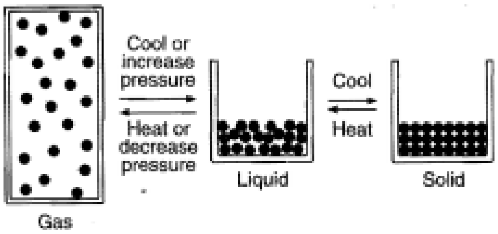


Fig. 4.1 Schematic representation of states of matter

Some common characteristics of three forms of matter are summarised below:

S.No.	Gases	Liquids	Solids
1.	No definite shape; can fill uniformly any volume available; have indefinite volume.	No definite shape, *i.e.,* assume the shape of the container; have definite volume.	Have definite shape and definite volume.
2.	Extremely disordered particles; much empty space; particles have random motion; intermolecular attraction very small but high kinetic energies (particles are free to move in all directions).	Disordered clusters of particles; quite close to each other; random motion; considerable intermolecular attraction; kinetic energy is less (particles free to move but always remain in contact with each other).	Ordered arrangement of particles; distances between the particles are very small and fixed. Intermolecular forces are high; vibrational motion only.
3.	Low density.	Intermediate density.	High density.
4.	Compressible.	Slightly compressible.	Nearly incompressible.
5.	Fluid, diffuse rapidly.	Fluid; diffuse through other liquids.	Not fluid; diffuse very slowly only through solids.

SECTION 1 : GASEOUS STATE

4.2 THE GASEOUS STATE

Of the three states of matter, the gaseous state is the simplest and shows greatest uniformity in behaviour. Gases have the following general characteristics:

(i) Gases are highly compressible. These can be compressed into smaller volumes, *i.e.*, increasing their densities by applying increased pressure.

(ii) Gases expand without limit. A gas sample can occupy completely and uniformly the volume of any container.

(iii) Gases exert pressure on the walls of the container uniformly in all directions.

(iv) Gases diffuse rapidly through each other to form a homogeneous mixture. Conversely, different gases in a mixture like air do not separate on standing.

(v) The characteristics of gases are described fully in terms of **four parameters** (measurable properties):

(a) the volume, V, of the gas

(b) its pressure, P

(c) its temperature, T

(d) the amount of the gas (*i.e.*, mass or number of moles).

(a) The volume of the container is the volume of the gas sample. Volume is expressed in litre (L), millilitre (mL) or cubic centimetre (cm^3) or cubic metre (m^3).

$$1\text{ L} = 1000\text{ mL};\ 1\text{ mL} = 10^{-3}\text{ L}$$

$$1\text{ L} = 1\text{ dm}^3;\quad 1\text{ dm}^3 = 10^3\text{ cm}^3$$

$$1\text{ m}^3 = 10^3\text{ dm}^3 = 10^6\text{ cm}^3 = 10^6\text{ mL} = 10^3\text{ L}$$

(b) The pressure of the gas is the force exerted by the gas per unit area of the walls of the container. The pressure of gases is measured by a device known as manometer. Two types of manometers, open-end manometer and closed-end manometer, are commonly used to measure gaseous pressure.

Pressure of one atmosphere (1 atm) is defined as the pressure that can support a column of mercury of 76 cm height at 0°C (density of mercury = 13.5951 g cm^{-3}) and at standard gravity = 980.665 cm s^{-2}. One atmosphere is also referred to as 760 torr.

$$1\text{ atm} = 76.0\text{ cm of mercury} = 760\text{ mm of mercury}$$

$$= 760\text{ torr}$$

SI unit of pressure is pascal (Pa) which is defined as the pressure exerted when a force of 1 newton acts on a 1 m^2 area.

$$1\text{ atm} = 101.325 \times 10^3\text{ N m}^{-2} = 101.325\text{ kPa}$$

An older unit of pressure is 'bar' which is equal to 10^5 Pa.

(c) The temperature of the gas is measured in centigrade degree (°C) or celsius degree with the help of thermometers.

SI unit of temperature is **Kelvin** (K) or **absolute degree.**

$$K = °C + 273$$

(d) Mass of gas is expressed in gram or kilogram.

$$1\text{ kg} = 10^3\text{ g}$$

The mass of the gas is also expressed in number of moles.

$$\text{moles of gas } (n) = \frac{\text{Mass in grams}}{\text{Molar mass}} = \frac{m}{M}$$

(vi) All gases obey certain laws called **gas laws.**

4.3 GAS LAWS

(i) Boyle's law: It relates the volume and the pressure of a given mass of a gas at constant temperature.

The relationship between the volume and the pressure of a gas was studied by **Robert Boyle** in 1662. He found that increasing the pressure at constant temperature on a sample of a gas causes the volume of the gas to decrease proportionately, *i.e.*, if the pressure is doubled, the volume becomes half and so on. Boyle's law states that **at constant temperature, the volume of a sample of a gas varies inversely with the pressure.**

$$V \propto \frac{1}{P} \quad \text{(when temperature is kept constant)}$$

The proportionality can be changed into an equality by introducing a constant, k, *i.e.*,

$$V = \frac{k}{P} \text{ or } PV = k$$

Alternatively, Boyle's law can also be stated as follows:

Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant.

The value of the constant depends upon the amount of a gas and the temperature.

Mathematically, it can be written as,

$$P_1V_1 = P_2V_2 = P_3V_3 = \ldots$$

Boyle's law can be verified by any one of the following three ways graphically (Fig. 4.2):

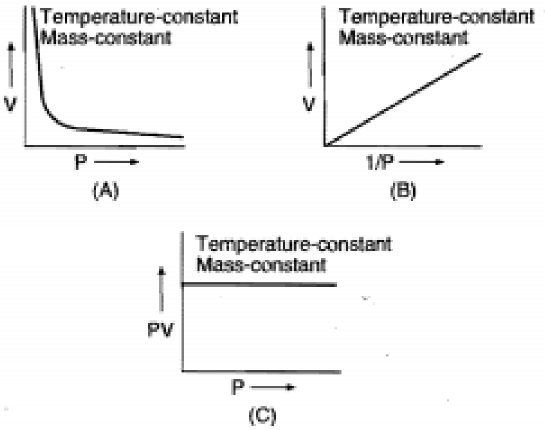


Fig. 4.2

The first curve shows the variation of volume of a given mass of gas with pressure at constant temperature. The shape of the curve is rectangular hyperbola. This curve is also called **isotherm.**

The second curve showing the relationship between volume and reciprocal of pressure is a straight line. It confirms the statement that at constant temperature, volume of a given mass of gas is inversely proportional to the pressure. The third curve shows a straight line parallel to pressure-axis. This confirms that the product of pressure and volume of a given mass of a gas at constant temperature is constant.

Location of straight line and curve changes with temperature in the isotherm.

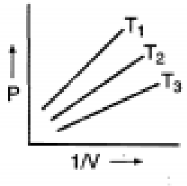


Fig. 4.2(D)

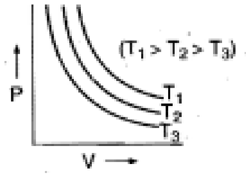


Fig. 4.2(E)

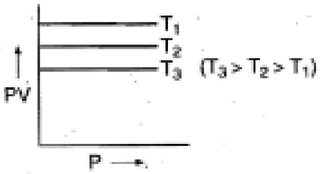


Fig. 4.2(F)

According to Boyle's law, PV = constant at constant temperature

$$\therefore \log P + \log V = \text{constant}$$

$$\log P = -\log V + \text{constant}$$

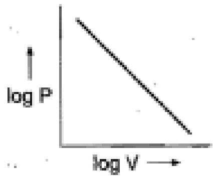


Fig. 4.2(G)

(ii) Charles' law: It relates the volume and temperature of a given mass of a gas at constant pressure.

Experiments have shown that when 273 mL sample of a gas at 0°C is heated to 1°C, its volume increases by 1 mL, *i.e.*, it becomes 274 mL. At 10°C, the volume increases to 283 mL if the pressure remains constant in both cases. Similarly, when 273 mL sample of gas at 0°C is cooled to –1°C, its volume decreases to 272 mL while at –10°C, the volume decreases to 263 mL if the pressure remains constant.

Thus, all gases expand or contract by the same fraction of their volumes at 0°C per degree change of temperature, *i.e.*, for each degree change of temperature, the volume of a sample of a gas changes by the fraction $\frac{1}{273}$ of its volume at 0°C.

Let the volume of a given amount of a gas be V_0 at 0°C. The temperature is increased by t° C and the new volume becomes V_t.

Thus, $$V_t = V_0 + \frac{V_0}{273} \times t = V_0\left(1 + \frac{t}{273}\right)$$

or $$V_t = V_0\left(\frac{273 + t}{273}\right) \qquad \text{... (i)}$$

A new temperature scale was introduced known as **Kelvin scale** or **absolute scale** named after the British physicist and mathematician **Lord Kelvin.** The lower limit of the scale is called absolute zero which corresponds to –273°C. At absolute zero or – 273° C, all molecular motions would stop and the volume of the gas would become zero. The gas would become a liquid or solid. Thus, **absolute zero is that temperature at which no substance exists in the gaseous state.** The temperature in absolute is always obtained by adding 273 to the temperature expressed in °C.

$$\text{K} = (°\text{C} + 273)$$

This new temperature scale may be used for deducing Charles' law.

By substituting T for $273 + t$ and T_0 for 273 in Eq. (i),

$$V_t = \frac{V_0 \times T}{T_0}$$

or $$\frac{V_t}{T} = \frac{V_0}{T_0}$$

or $$\frac{V}{T} = \text{constant (if pressure is kept constant)}$$

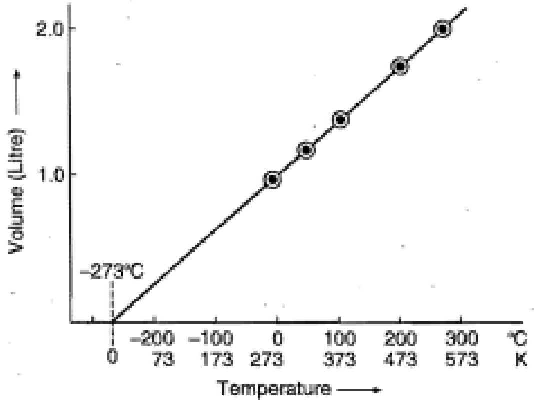


Fig. 4.3

This is Charles' law. It can be stated as follows:

The volume of a given amount of a gas at constant pressure varies directly as its absolute temperature.

$$V \propto T \quad \text{(if pressure is kept constant)}$$

Charles' law can be verified experimentally by plotting the values of volumes of a given amount of a gas under respective absolute temperatures at constant pressure. The straight line confirms the above statement.

(iii) Pressure-temperature law: It relates the pressure and absolute temperature of a given mass of a gas at constant volume.

Volume remaining constant, the pressure of a given mass of a gas increases or decreases by $\frac{1}{273}$ of its pressure at 0°C per degree change of temperature.

$$P_t = P_0 + \frac{P_0 \times t}{273}$$

or $$P_t = P_0\left(1 + \frac{t}{273}\right)$$

or $$P_t = P_0\left(\frac{273+t}{273}\right) = P_0\,\frac{T}{T_0}$$

or $$\frac{P_t}{T} = \frac{P_0}{T_0}$$

or $$P \propto T \quad \text{(if volume is kept constant)}$$

At constant volume, the pressure of a given amount of a gas is directly proportional to its absolute temperature.

4.4 IDEAL GAS EQUATION

This equation is obtained by combining Boyle's and Charles' laws.

$$V \propto \frac{1}{P} \quad \text{... (i) (at constant temperature and definite mass)}$$

$$V \propto T \quad \text{... (ii) (at constant pressure and definite mass)}$$

Combining eqs. (i) and (ii), we get

$$V \propto \frac{T}{P} \qquad \text{(for definite mass)}$$

$$\frac{PV}{T} = \text{constant} \qquad \text{... (iii)}$$

From the above relation, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \text{... (iv)}$$

From eq. (iii),

$$\frac{PV}{T} = R$$

or $$PV = RT \quad \text{for 1 mole gas}$$

$$PV = nRT \quad \text{for } n \text{ mole gas} \qquad \text{... (v)}$$

When mass of the gas is taken in grams, the value of n will be given by:

$$n = \frac{\text{Mass of the gas in gram}}{\text{Mol. mass of the gas in gram}}$$

Let w and M be the mass and molecular mass of a gas; then

$$n = \frac{w}{M}$$

Hence, eq. (v) becomes

$$PV = \frac{w}{M}RT \qquad \text{... (vi)}$$

or $$P = \frac{w}{M}\cdot\frac{RT}{V} \quad \left[\frac{w}{V} = \frac{\text{Mass}}{\text{Volume}} = \text{Density } (d)\right]$$

or $$P = \frac{d}{M}RT \qquad \text{... (vii)}$$

Eqs. (vi) and (vii) are modified forms of gas equation. The above equations are strictly followed by ideal gases.

Nature of Molar Gas Constant *R*

Gas equation for one gram mole,

$$PV = RT$$

or $$R = \frac{P \times V}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{\text{Force}}{(\text{Length})^2}$$

$$\text{Volume} = (\text{Length})^3$$

So, $$R = \frac{\dfrac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Temperature}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Temperature}}$$

$$= \frac{\text{Work}}{\text{Temperature}}$$

Thus, the value of R should always be expressed in units of work per degree kelvin per mole.

Numerical Values of *R*

$$R = \frac{PV}{T}$$

One gram mole of a gas at one atmospheric pressure and 0°C (273 K) occupies a volume 22.4 litre.

$P = 1$ atmosphere, $T = 273$ K, $V = 22.4$ litre

So, $$R = \frac{1 \times 22.4}{273}$$

$$= 0.0821 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$$

If pressure is taken in dyne/cm^2 and volume in mL,

$P = 76 \times 13.67 \times 981$ dyne/cm^2, $V = 22400$ mL for 1 mole,

$T = 273$ K

So, $$R = \frac{76 \times 13.67 \times 981 \times 22400}{273}$$

$$= 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

Since, 1 joule $= 10^7$ erg, so

$$R = 8.314 \text{ joule K}^{-1} \text{ mol}^{-1}$$

Since, 1 calorie $= 4.184 \times 10^7$ erg, so

$$R = \frac{8.314 \times 10^7}{4.184 \times 10^7}$$

$$= 1.987 \approx 2 \text{ calorie K}^{-1} \text{ mol}^{-1}$$

Note: Although, R can be expressed in different units, but for pressure-volume calculations, R must be taken in the same units of pressure and volume.

Barometric Distribution

In the case of ordinary gases, pressure in the container is unaffected by the gravitational field. But in high molecular mass polymeric gases, pressure varies with height.

Let P_0 be the pressure at ground level and P be the pressure at height 'h'; then

$$2.303 \log_{10}\left(\frac{P}{P_0}\right) = -\left\{\frac{Mgh}{R}\right\}$$

Similarly for density and number of moles the equation may be given as:

$$2.303 \log_{10}\left(\frac{d}{d_0}\right) = -\left\{\frac{Mgh}{R}\right\}$$

$$2.303 \log_{10}\left(\frac{n}{n_0}\right) = -\left\{\frac{Mgh}{R}\right\}$$

These relations are valid under isothermal conditions for density, pressure and number of moles.

If temperature is not constant then the relations of barometric distribution may be given as,

$$2.303 \log_{10}\left(\frac{P}{P_0}\right) = -\frac{Mgh}{RT}$$

$$2.303 \log_{10}\left(\frac{n}{n_0}\right) = -\frac{Mgh}{RT}$$

Open vessel concept: In open vessel of a gas, pressure and volume are always constant.

$$\therefore \qquad PV = n_1RT_1 \qquad \ldots (1)$$

$$PV = n_2RT_2 \qquad \ldots (2)$$

Here, n_1 and n_2 are number of moles at temperatures T_1 and T_2.

Dividing eq. (1) by (2), we get

$$n_1T_1 = n_2T_2$$

Dry and moist gas: If volume under moist condition is given then volume of dry gas can be determined.

$$P_{\text{moist}}V_{\text{moist}} = P_{\text{dry}}V_{\text{dry}}$$

$$P_{\text{dry}} = P_{\text{moist}} - \text{Aqueous tension or vapour pressure of water}$$

$$\text{Relative humidity} = \frac{\text{Partial pressure of water in air}}{\text{Vapour pressure of water}}$$

Payload (Lifting Capacity of Balloon)

When a balloon is filled with lighter gas like H_2 and He (lighter than air) then it rises up due to the difference in the density of air and the gas. Payload or lifting capacity of balloon may be calculated as:

$$\text{Pay Load} = \begin{bmatrix}\text{Mass of air filled}\\ \text{in the balloon}\end{bmatrix} - \begin{bmatrix}\text{Mass of gas filled in the}\\ \text{balloon at same tempera -}\\ \text{ture and pressure}\end{bmatrix} - \begin{bmatrix}\text{Mass of}\\ \text{balloon}\end{bmatrix}$$

SOME SOLVED EXAMPLES

Example 1. *A sample of a gas occupies 10 litre under a pressure of 1 atmosphere. What will be its volume if the pressure is increased to 2 atmosphere? Assume that the temperature of the gas sample does not change.*

Solution: $V_1 = 10 \text{ litre} \quad V_2 = ?$

$P_1 = 1 \text{ atm} \quad P_2 = 2 \text{ atm}$

Applying Boyle's law,

$$P_1V_1 = P_2V_2$$

So,

$$V_2 = \frac{P_1V_1}{P_2} = \frac{1 \times 10}{2} = 5 \text{ litre}$$

Example 2. *A sample of a gas occupies 600 mL at 27°C and 1 atm. What will be the volume at 127°C if the pressure is kept constant?*

Solution: $V_1 = 600 \text{ mL} \quad T_1 = 27 + 273 = 300 \text{ K}$

$V_2 = ? \quad T_2 = 127 + 273 = 400 \text{ K}$

Applying Charles' law, $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

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

$$= \frac{600 \times 400}{300}$$

$$= 800 \text{ mL}$$

Example 3. *A gas cylinder containing cooking gas can withstand a pressure of 14.9 atmosphere. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C. Due to a sudden fire in the building, the temperature starts rising. At what temperature will the cylinder explode?*

Solution: Since, the gas is confined in a cylinder, its volume will remain constant.

Initial conditions	Final conditions
$P_1 = 12 \text{ atm}$	$P_2 = 14.9 \text{ atm}$
$T_1 = 27 + 273 = 300 \text{ K}$	$T_2 = ?$

Applying pressure-temperature law,

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

So,

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

$$= \frac{14.9 \times 300}{12} = 372.5 \text{ K}$$

$$\text{Temperature in } ^\circ\text{C} = (372.5 - 273) = 99.5^\circ \text{C}$$

Example 4. *A 1000 mL sample of a gas at −73°C and 2 atmosphere is heated to 123°C and the pressure is reduced to 0.5 atmosphere. What will be the final volume?*

Solution:

Initial conditions	Final conditions
$P_1 = 2 \text{ atm}$	$P_2 = 0.5 \text{ atm}$
$V_1 = 1000 \text{ mL}$	$V_2 = ?$
$T_1 = -73^\circ \text{C} = (-73 + 273)$ $= 200 \text{ K}$	$T_2 = 123^\circ \text{C} = (123 + 273)$ $= 400 \text{ K}$

We know that,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

So,

$$\frac{2 \times 1000}{200} = \frac{0.5 \times V_2}{400}$$

or

$$V_2 = \frac{2 \times 1000 \times 400}{200 \times 0.5}$$

$$= 8000 \text{ mL}$$

Example 5. *A sample of a gas occupies a volume of* 512 *mL at* 20°*C and* 74 *cm of Hg as pressure. What volume would this gas occupy at STP?*

Solution:

Initial conditions	Final conditions (STP)
$P_1 = 74$ cm	$P_2 = 76$ cm
$T_1 = 20° \text{C} = (20 + 273) = 293 \text{ K}$,	$T_2 = 0° \text{C} = 273 \text{ K}$
$V_1 = 512$ mL	$V_2 = ?$

We know that,

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{74 \times 512}{293} = \frac{76 \times V_2}{273}$$

So,

$$V_2 = \frac{74 \times 512 \times 273}{293 \times 76}$$

$$= 464.5 \text{ mL}$$

Example 6. 3.7 *g of a gas at* 25°*C occupied the same volume as* 0.184 *g of hydrogen at* 17°*C and at the same pressure. What is the molecular mass of the gas?*

Solution: For hydrogen,

$w = 0.184$ g ; $T = 17 + 273 = 290$ K; $M = 2$

We know that, $PV = \frac{w}{M} RT$

$$= \frac{0.184}{2} \times R \times 290 \qquad \text{... (i)}$$

For unknown gas,

$w = 3.7$ g; $T = 25 + 273 = 298$ K; $M = ?$

$$PV = \frac{3.7}{M} \times R \times 298 \qquad \text{... (ii)}$$

Equating both the equations,

$$\frac{3.7}{M} \times R \times 298 = \frac{0.184}{2} \times R \times 290$$

or

$$M = \frac{3.7 \times 298 \times 2}{0.184 \times 290} = 41.33$$

Example 7. *What is the pressure of HCl gas at* –40°*C if its density is* 8.0 *kg* m^{-3}*?* ($R = 8.314\ J\ K^{-1}\ mol^{-1}$)

Solution: Equation for ideal gas,

$$PV = \frac{w}{M} RT$$

or

$$P = \frac{w}{V} \times \frac{RT}{M}$$

$$= d \times \frac{RT}{M} \qquad \left(\frac{w}{V} = \text{density} = d\right)$$

Given, $d = 8.0 \text{ kg m}^{-3}$; $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$;

$$T = -40 + 273 = 233 \text{ K}$$

and $M = 36.5 \text{ g mol}^{-1} = 36.5 \times 10^{-3} \text{ kg mol}^{-1}$

Substituting the values in the above equation,

$$P = \frac{8.0 \times 8.314 \times 233}{36.5 \times 10^{-3}} = 424.58 \times 10^3 \text{ Pa}$$

Example 8. *A certain quantity of a gas occupies* 100 *mL when collected over water at* 15°*C and* 750 *mm pressure. It occupies* 91.9 *mL in dry state at NTP. Find the aqueous vapour pressure at* 15°*C.*

Solution: Let the aqueous vapour pressure be *p* mm.

Initial conditions	NTP conditions
P_1 (dry gas) $= (750 - p)$ mm	$P_2 = 760$ mm
$V_1 = 100$ mL	$V_2 = 91.9$ mL
$T_1 = 15 + 273 = 288$ K	$T_2 = 273$ K

Applying gas equation,

$$\frac{(750 - p) \times 100}{288} = \frac{760 \times 91.9}{273}$$

or

$$750 - p = \frac{760 \times 91.9 \times 288}{100 \times 273}$$

$$= 736.8 \text{ mm}$$

$$p = 750 - 736.8$$

$$= 13.2 \text{ mm}$$

Example 9. *A balloon of diameter* 20 *m weighs* 100 *kg. Calculate its payload if it is filled with helium at* 1.0 *atm and* 27°*C. Density of air is* 1.2 *kg* m^{-3}.
($R = 0.082\ dm^3\ atm\ K^{-1}\ mol^{-1}$) **(IIT 1994)**

Solution:

$$\text{Volume of balloon} = \frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7} \times (10)^3 = 4190.47 \text{ m}^3$$

$$\text{Mass of the air displaced} = 4190.47 \times 1.2 = 5028.56 \text{ kg}$$

$$\text{No. of moles of helium in the balloon} = \frac{PV}{RT}$$

$$= \frac{1 \times 4190.47 \times 10^3}{0.082 \times 300} = 170344$$

$$\text{Mass of helium} = 4 \times 170.344 \times 10^3 \text{ g} = 681.376 \text{ kg}$$

$$\text{Mass of filled balloon} = 681.376 + 100 = 781.376 \text{ kg}$$

$$\text{Payload} = \text{Mass of air displaced} - \text{Mass of filled balloon}$$

$$= 5028.56 - 781.376 = 4247.184 \text{ kg}$$

$$4 = \sqrt{\frac{32}{M_{gas}}} \text{ or } 16 = \frac{32}{M_{gas}}$$

or $M_{gas} = \frac{32}{16} = 2$, *i.e.*, H_2]

12. The rates of diffusion of hydrogen and deuterium are in the ratio:

(a) 1 : 1 (b) $\sqrt{2} : 1$ (c) 4 : 1 (d) 1 : 4

[**Ans.** (b)]

[**Hint:** $\frac{r_{H_2}}{r_{D_2}} = \sqrt{\frac{M_{D_2}}{M_{H_2}}}$

$$\frac{r_{H_2}}{r_{D_2}} = \sqrt{\frac{4}{2}}$$

$r_{H_2} = \sqrt{2} r_{D_2}$]

13. The time taken for effusion of 64 mL of oxygen will be same as the time taken for the effusion of which of the following gases under identical conditions?

(a) 64 mL of H_2 (b) 100 mL of N_2

(c) 64 mL of CO_2 (d) 45.24 mL of SO_2

[**Ans.** (d)]

[**Hint:** $\frac{r_{O_2}}{r_{gas}} = \sqrt{\frac{M_{gas}}{M_{O_2}}}$

$\frac{64}{V} = \sqrt{\frac{64}{32}}$ or $V = \frac{64}{\sqrt{2}} = 45.25$ mL]

14. Which of the following pairs of gases will have identical rate of effusion under similar conditions?

(a) Diprotium and dideuterium

(b) Carbon dioxide and ethane

(c) Dideuterium and helium

(d) Ethene and ethane

[**Ans.** (c)]

[**Hint:** Dideuterium and helium have same molar mass, hence they will diffuse with identical rate under identical conditions.]

15. Two gas bulbs *A* and *B* are connected by a tube having a stopcock. Bulb *A* has a volume of 100 mL and contains hydrogen. After opening the gas from *A* to the evacuated bulb *B*, the pressure falls down to 40%. The volume (mL) of *B* must be: **[PET (Kerala) 2006]**

(a) 75 (b) 150 (c) 125 (d) 200

(e) 250

[Ans. (b)]

[**Hint:** $P_1V_1(A) + P_2V_2(B) = P_R(V_1 + V_2)$

$100 \times 100 + 0 \times V_2 = 40(100 + V_2)$

$V_2 = 250 - 100 = 150$ mL]

4.7 KINETIC THEORY OF GASES

This theory was a generalization for about ideal gases. It was presented by **Bernoulli** in 1738 and developed in 1860 by Clausius, Maxwell, Kroning and Boltzmann. Postulates of kinetic theory of gases are:

(1) Gases are made up of small structural units called atc or molecules. Volume of individual atom or molecule considered negligible.

(2) Gas molecules are always in rapid random mot colliding with each other and with the wall of container.

(3) Collision among gas molecules is perfectly elastic, there is no loss in kinetic energy and moment during s collision.

(4) Gas molecules neither attract nor repel each other.

(5) Pressure exerted by gas is due to collisions of molecules with the wall of the container.

Pressure ∝ Number of collisions per unit time per unit area by the molecules on the wall of the container

(6) Kinetic energy of gas molecules depends only on absol temperature.

Kinetic energy ∝ absolute temperature

(7) The force of gravity has no effect on the speed of molecules.

Derivation of Kinetic Gas Equation

On the basis of the postulates of kinetic theory of gases, i possible to derive the mathematical expression, commc known as kinetic gas equation, *i.e.*,

$$PV = \frac{1}{3} mnc^2$$

where, P = pressure of the gas, V = volume of the gas, m = m of a molecule, n = number of molecules present in the gi amount of a gas and c = root mean square speed.

The root mean square speed (rms speed) may be defined as square root of the mean of squares of the individual speed o the molecules.

$$\text{rms speed} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \ldots + c_n^2}{n}}$$

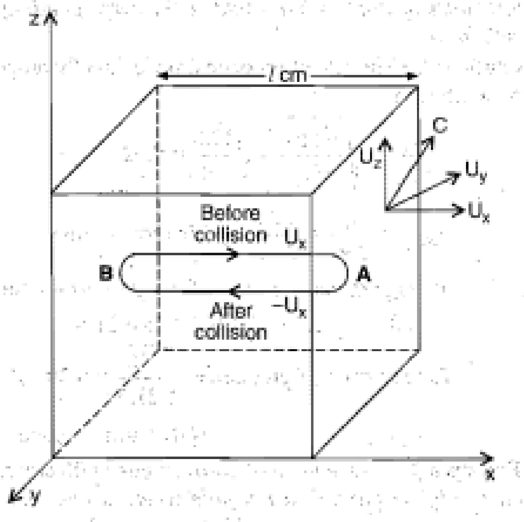
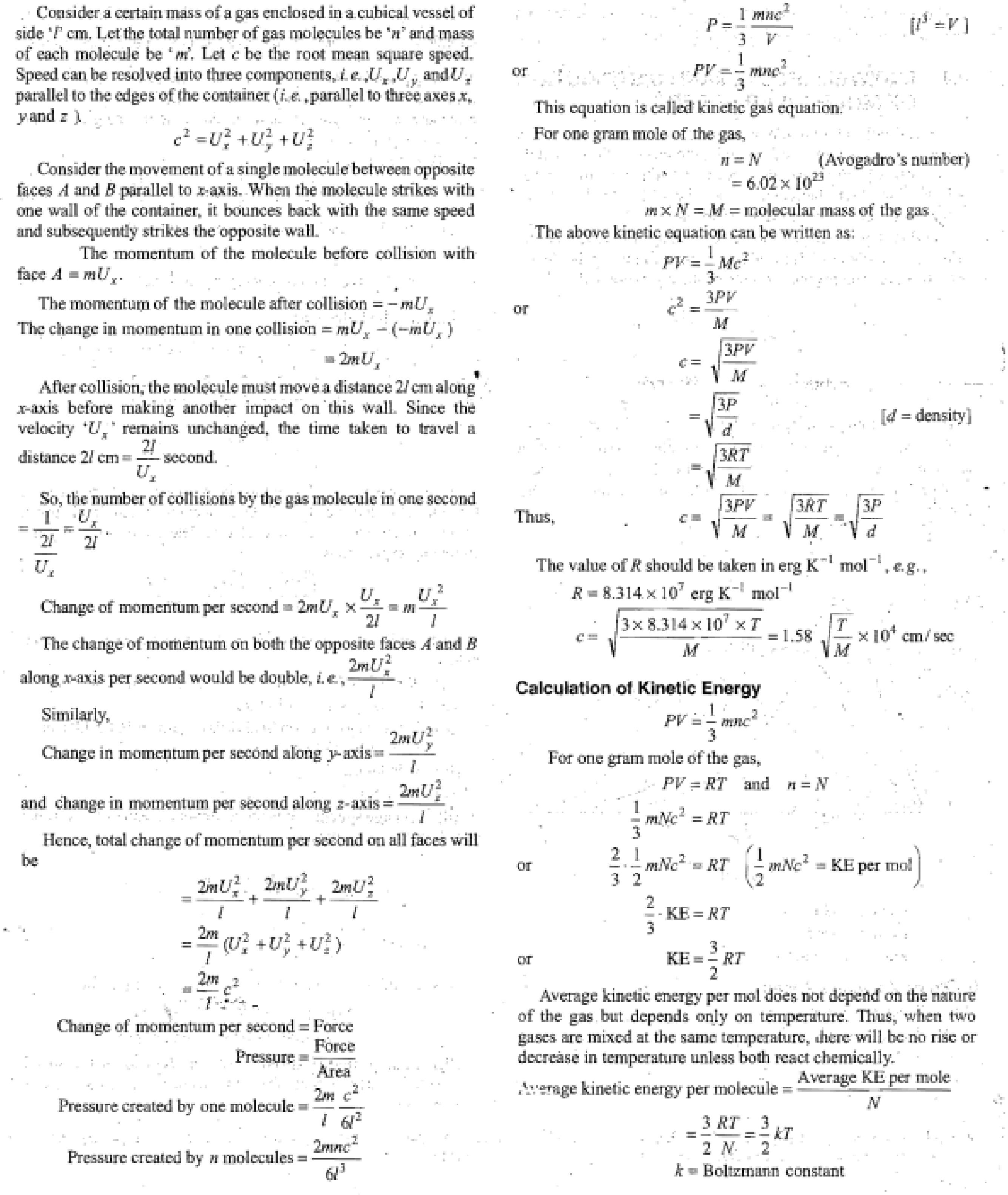


Fig. 4.5



Consider a certain mass of a gas enclosed in a cubical vessel of side 'l' cm. Let the total number of gas molecules be 'n' and mass of each molecule be 'm'. Let c be the root mean square speed. Speed can be resolved into three components, *i.e.*, U_x, U_y and U_z parallel to the edges of the container (*i.e.*, parallel to three axes x, y and z).

$$c^2 = U_x^2 + U_y^2 + U_z^2$$

Consider the movement of a single molecule between opposite faces A and B parallel to x-axis. When the molecule strikes with one wall of the container, it bounces back with the same speed and subsequently strikes the opposite wall.

The momentum of the molecule before collision with face $A = mU_x$.

The momentum of the molecule after collision $= -mU_x$

The change in momentum in one collision $= mU_x - (-mU_x)$

$$= 2mU_x$$

After collision, the molecule must move a distance $2l$ cm along x-axis before making another impact on this wall. Since the velocity 'U_x' remains unchanged, the time taken to travel a distance $2l$ cm $= \frac{2l}{U_x}$ second.

So, the number of collisions by the gas molecule in one second

$$= \frac{1}{\frac{2l}{U_x}} = \frac{U_x}{2l}.$$

Change of momentum per second $= 2mU_x \times \frac{U_x}{2l} = m\frac{U_x^2}{l}$

The change of momentum on both the opposite faces A and B along x-axis per second would be double, *i.e.*, $\frac{2mU_x^2}{l}$.

Similarly,

Change in momentum per second along y-axis $= \frac{2mU_y^2}{l}$

and change in momentum per second along z-axis $= \frac{2mU_z^2}{l}$

Hence, total change of momentum per second on all faces will be

$$= \frac{2mU_x^2}{l} + \frac{2mU_y^2}{l} + \frac{2mU_z^2}{l}$$

$$= \frac{2m}{l}(U_x^2 + U_y^2 + U_z^2)$$

$$= \frac{2m}{l}c^2$$

Change of momentum per second = Force

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

Pressure created by one molecule $= \frac{2m}{l}\frac{c^2}{6l^2}$

Pressure created by n molecules $= \frac{2mnc^2}{6l^3}$

$$P = \frac{1}{3}\frac{mnc^2}{V} \qquad [l^3 = V]$$

or

$$PV = \frac{1}{3}mnc^2$$

This equation is called kinetic gas equation.

For one gram mole of the gas,

$$n = N \qquad \text{(Avogadro's number)}$$

$$= 6.02 \times 10^{23}$$

$$m \times N = M = \text{molecular mass of the gas}$$

The above kinetic equation can be written as:

$$PV = \frac{1}{3}Mc^2$$

or

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

$$c = \sqrt{\frac{3PV}{M}}$$

$$= \sqrt{\frac{3P}{d}} \qquad [d = \text{density}]$$

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

Thus,

$$c = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

The value of R should be taken in erg K^{-1} mol^{-1}, *e.g.*,

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$c = \sqrt{\frac{3 \times 8.314 \times 10^7 \times T}{M}} = 1.58\sqrt{\frac{T}{M}} \times 10^4 \text{ cm/sec}$$

Calculation of Kinetic Energy

$$PV = \frac{1}{3}mnc^2$$

For one gram mole of the gas,

$$PV = RT \quad \text{and} \quad n = N$$

$$\frac{1}{3}mNc^2 = RT$$

or

$$\frac{2}{3}\cdot\frac{1}{2}mNc^2 = RT \quad \left(\frac{1}{2}mNc^2 = \text{KE per mol}\right)$$

$$\frac{2}{3}\cdot\text{KE} = RT$$

or

$$\text{KE} = \frac{3}{2}RT$$

Average kinetic energy per mol does not depend on the nature of the gas but depends only on temperature. Thus, when two gases are mixed at the same temperature, there will be no rise or decrease in temperature unless both react chemically.

Average kinetic energy per molecule $= \frac{\text{Average KE per mole}}{N}$

$$= \frac{3}{2}\frac{RT}{N} = \frac{3}{2}kT$$

k = Boltzmann constant

The ratio R/N is constant and is known as Boltzmann constant. Its numerical value is 1.38 × 10^{-16} erg K^{-1} molecule^{-1}.