

GASESSTATES OF MATTER:-

∴ Matter exists in four states. These are:-  
 (i) SOLID (ii) LIQUID (iii) GAS (iv) PLASMA

The simplest form of matter is gaseous state. Liquids are less common than gases, solids or plasmas. The reason is that liquid state can exist only in a narrow range of temperature and pressure. Most of the matter around us is in solid state. Plasma is called fourth state of matter. 99% of known universe is in plasma state.

PROPERTIES OF GASES:-VOLUME OF GASES

(1) Gases do not have a definite volume, they occupy all the available space. The volume of gas is volume of container.

(2) SHAPE OF GASES: The gases do not have definite shape. They take shape of container just like liquids.

(3) DENSITIES OF GASES: Gases have very low densities. Due to low densities of gases as compared to liquids and solids gases can be bubbled through liquids, and they tend to rise up.

(4) DIFFUSION & EFFUSION: Gases can diffuse and effuse. This property also operates in liquids but negligible in solids.

(5) COMPRESSIBILITY: Gases can be compressed by applying pressure. It is due to large empty spaces between their molecules.

(6) EXPANSION: Gases can expand on heating or by increasing the available volume. Liquids or solids do not show considerable increase in volume when they are heated.

(7) JOULE THOMSON EFFECT: When a highly compressed gas is allowed to cool expand suddenly cooling takes place. It is called Joule Thomson effect.

8. PRESSURE: Gases exert pressure on the walls of container. Gas molecules are constantly moving in random directions they collide on the walls of container. The pressure of gas is due to collisions of gas molecules on walls of container.

9. INTERMOLECULAR FORCES: There are very weak intermolecular forces in gases.

### PROPERTIES OF LIQUIDS:

1. SHAPE AND VOLUME: Liquids have no definite shape but they have definite volume. They adopt the shape of container. On the other hand solids have definite shape.
2. MOTION OF LIQUID MOLECULES: Liquid molecules are constantly moving. The evaporation and diffusion of liquids is due to motion of molecules.
3. DENSITIES: The densities of liquids are much greater than that of gases but close to those of solids.
4. INTERMOLECULAR SPACES: Just like solids, liquids have negligible intermolecular spaces.
5. INTERMOLECULAR FORCES: The intermolecular forces are intermediate between gases and solids. The m.p., B.P. of liquids and solids depend upon strength of intermolecular forces.
6. KINETIC ENERGY: Liquid molecules possess K.E. due to their motion. Liquids can be converted into solids by decreasing K.E.
7. COLLISIONS: Molecules of liquids collide with one another and exchange energies. Solid molecules cannot do so.

### PROPERTIES OF SOLIDS:

1. NON COMPRESSABLE: particles present in solids are very close to each other. They are tightly packed. Thus solids are non compressable. They cannot diffuse.
2. INTERMOLECULAR FORCES: There are strong attractive forces in solids. Thus solids have definite shape and volume.
3. VIBRATIONAL MOTION: Solid particles possess only vibrational motion.

# GAS LAWS

1. BOYLE'S LAW: It is defined as, "The volume of a given mass of a gas is inversely proportional to pressure applied to the gas at constant temperature. Mathematically it could be written as:- ~~is~~

$$V \propto \frac{1}{P} \quad (\text{AT CONSTANT TEMP. AND MASS})$$

$$V = k \frac{1}{P} \quad \text{K IS CALLED PROPORTIONALITY CONSTANT.}$$

The value "k" is different for different amount of the same gas. It is also different at different temp.

$$P \times V = k \quad \text{--- (1) (when T and n are constant)}$$

From Equation 1, Boyle's Law could be defined as "The product of pressure and vol. always remains constant at constant temp. & constant quantity of gas. Thus eq (1) can be written as

$$P_1 \times V_1 = k \quad \text{AND} \quad P_2 \times V_2 = k$$

$P_1 V_1$  and  $P_2 V_2$  and initial values of pressure and volume and final values of pressure & volume.

## EXPERIMENTAL VERIFICATION:-

Let us consider definite mass of gas present in a cylinder fitted with a movable piston. The cylinder is also fitted with a manometer to read pressure of gas directly. Let initial volume is  $1 \text{ dm}^3$  when initial pressure is 2 atm (due to 1 wt. of on piston). When volume of gas is reduced to one half ( $\frac{1}{2} \text{ dm}^3$ ) by adding two wts on piston, pressure becomes four Atmospheres. When volume is reduced to one third ( $\frac{1}{3} \text{ dm}^3$ ) by adding three equal wts. the pressure becomes 6 atm.

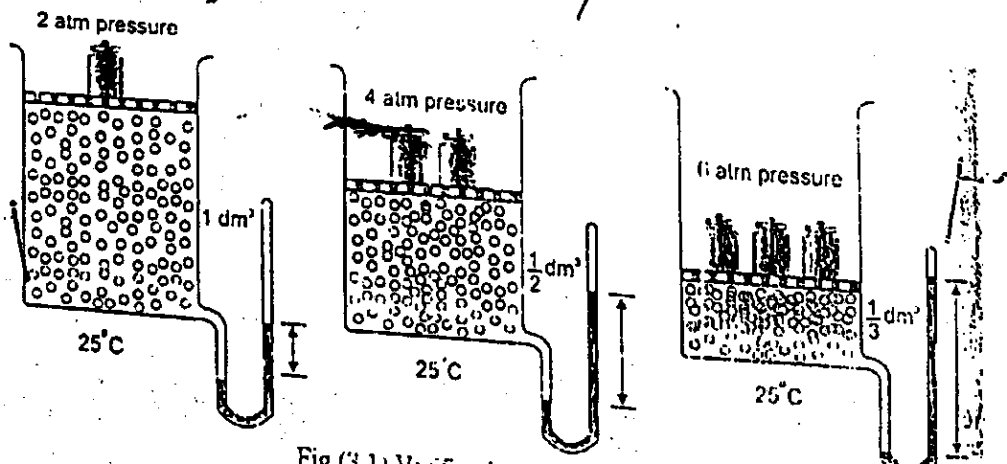


Fig (3.1) V vs P

It is found that

$$P_1 \times V_1 = k = 2 \times 1 = 2 \text{ atm dm}^3 = k$$

$$P_2 \times V_2 = k = 4 \times \frac{1}{2} = 2 \text{ atm dm}^3 = k$$

$$P_3 \times V_3 = k = 6 \times \frac{1}{3} = 2 \text{ atm dm}^3 = k$$

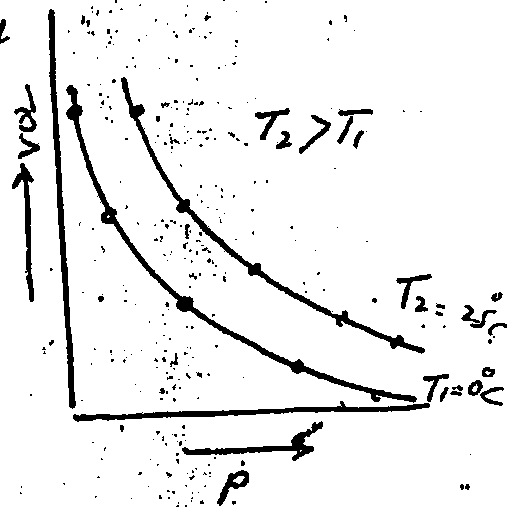
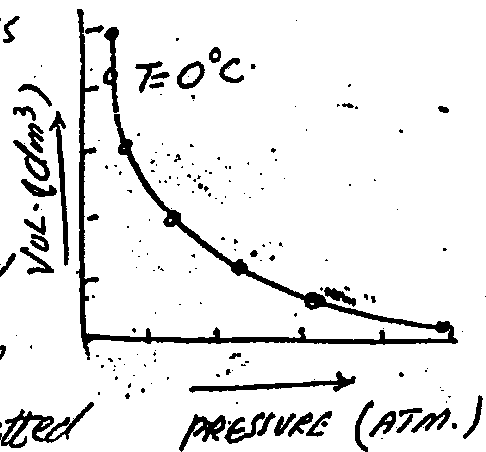
Thus it is concluded that product of pressure and volume always remains constant at constant "T" and "n".

### GRAPHICAL EXPLANATION OF BOYLE'S LAW.

Let us consider definite mass of a gas enclosed in a cylinder fitted with a movable piston. The volume of gas decreases by increasing pressure at constant temp. (say  $0^\circ\text{C}$ ). If a graph is plotted between pressure along X-axis (ORDINATE) and volume along Y-axis (Abscissa) a curve is obtained. It is called ISOTHERM.

Now if temperature of same mass of gas is increased to  $25^\circ\text{C}$  the volume of gas is increased.

The pressure of gas is increased by keeping temp  $25^\circ$  constant. The volume decreases the graph is plotted between pressure and volume. A new isotherm is obtained which is away from both axes.

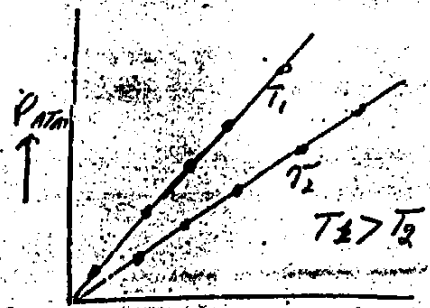


If another isotherm is drawn at further higher temperature, it also goes away from axes.

### GRAPH BETWEEN PRESSURE AND INVERSE OF VOLUME $\frac{1}{V}$

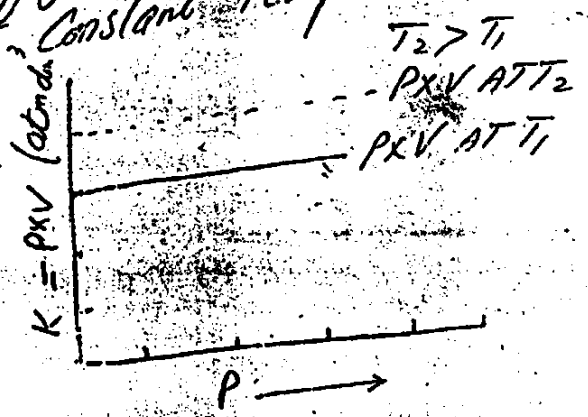
If a graph is plotted between inv. of volume ( $\frac{1}{V}$ ) along X-axis and pressure along Y-axis a straight line

is obtained. This shows that pressure and inverse of volume are directly proportional to each other. This straight line will meet at the origin which means that when pressure is very close to zero then volume is so high that inv. of volume is close to zero.



By increasing temperature of the same gas from  $T_1$  to  $T_2$  and keeping it constant at  $T_2$  we can vary pressure and volume. The graph of this data will give another straight line. This straight line will be closer to x-axis at low temp.

GRAPH BETWEEN PRESSURE AND PV  
 is plotted between "P" along x-axis and PV along y-axis a straight line parallel to x-axis is obtained which indicates that product of pressure and volume always remains constant at constant temperature. At some higher temp volume increases if pressure is kept constant. This value of PV at high temp is higher but constant.



The gas whose PV remains constant is called an ideal gas. But for real gases PV does not remain constant. Boyle's Law is applicable to an ideal gas.  
 SEE EXAMPLE NO. 1

# CHARLES'S LAW

It is a quantitative relationship between temperature and volume of a gas. It states that, "The volume of a given mass of a gas is directly proportional to absolute temperature at constant pressure. Mathematically it could be written as follows

$$V \propto T \text{ (at constant } P \text{ and Mass)}$$

$$V = kT \text{ (k is constant of proportionality)}$$

$$\frac{V}{T} = k \text{ --- (1)}$$

If temperature is changed from  $T_1$  to  $T_2$ , volume changes from  $V_1$  to  $V_2$ .

$$\frac{V_1}{T_1} = k$$

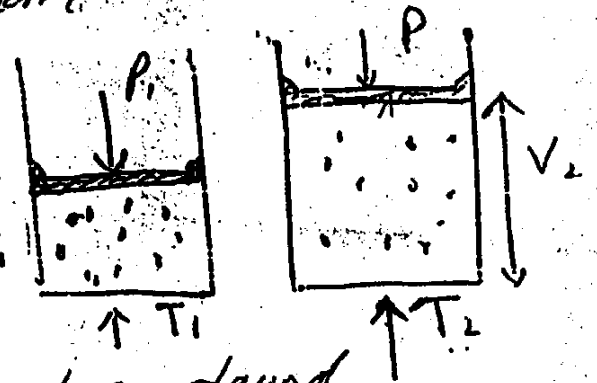
$$\frac{V_2}{T_2} = k$$

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

Equation (1) can be defined as "Ratio of volume and temp. always remains constant at const pressure".

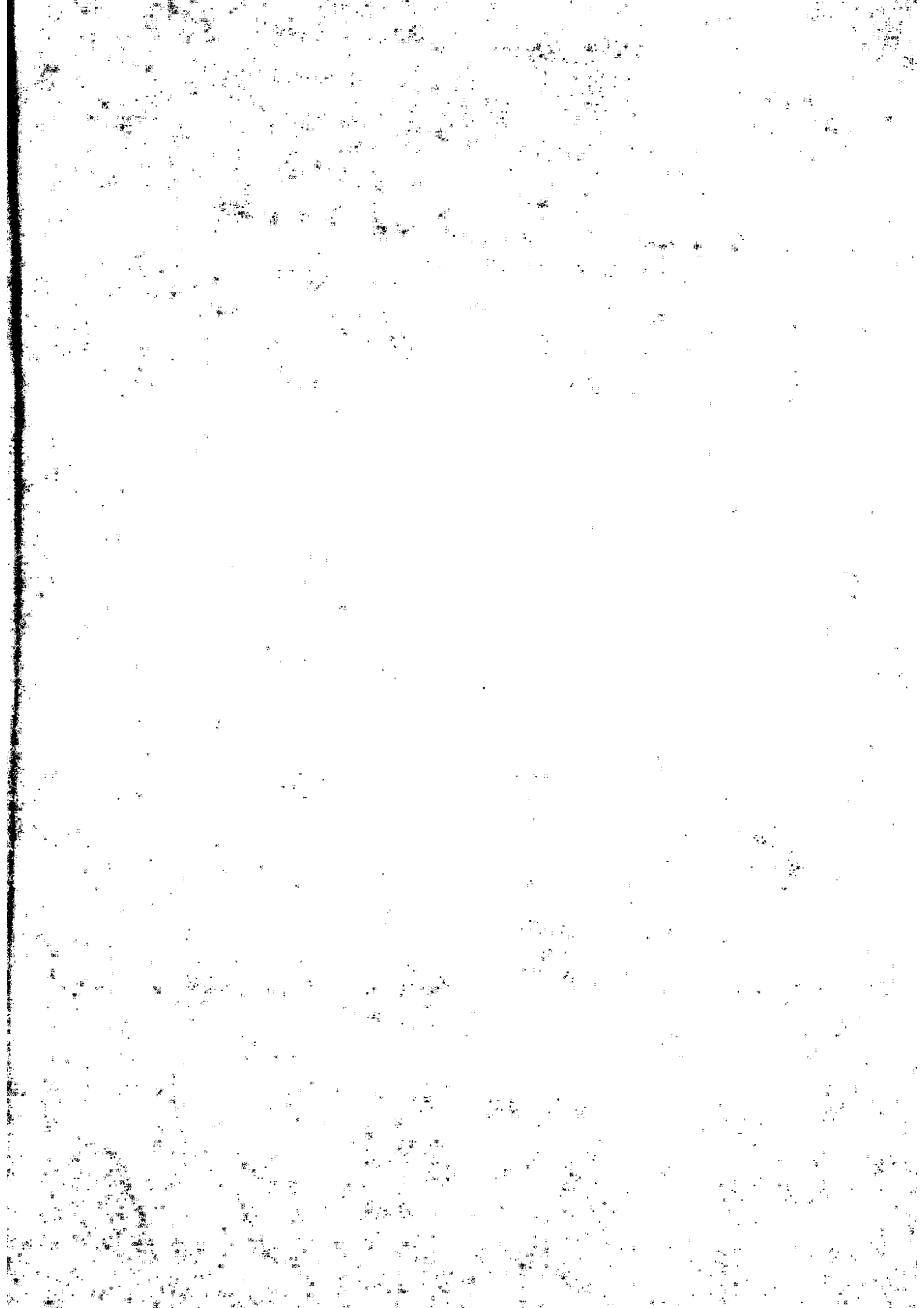
## EXPERIMENTAL VERIFICATION

Let us consider definite mass of a gas enclosed in a cylinder fitted with a movable piston. The volume of gas is  $V_1$  and Temp. is  $T_1$ . When gas is heated, both volume and temp. increase. Say volume becomes  $V_2$  and Temp. becomes  $T_2$ . It has been found



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

This verifies Charles's law.



New "R" is called universal gas constant

$$\frac{PV}{T} = R \quad \text{OR} \quad \frac{PV}{T} = \text{CONSTANT}$$

The equation can also be written as

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

### CALCULATION OF VALUE OF "R" WITH DIFFERENT UNITS.

The value of "R" is independent of nature of gas. It depends upon initial values of P, V, and "T" and units of these values.

Let us consider 1 mole of a gas at S.T.P.

- $n = 1 \text{ mole}$
- $P = 1 \text{ atm}$
- $V = 22.4 \text{ dm}^3$
- $T = 273 \text{ K}$

$$PV = nRT$$

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

$$\frac{1 \text{ atm} \times 22.4 \text{ dm}^3}{1 \text{ mole} \times 273 \text{ K}} = R$$

$$0.08205 \frac{\text{dm}^3 \cdot \text{atm}}{\text{mole K}} = R$$

If pressure is expressed in  $\text{N/m}^2$  and volume in " $\text{m}^3$ " then For 1 mole of gas at S.T.P

- $n = 1 \text{ mole}$
- $P = 101300 \text{ N/m}^2$
- $V = 0.0224 \text{ m}^3$
- $T = 273 \text{ K}$

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

$$\frac{101300 \text{ N} \times 0.0224 \text{ m}^3}{1 \text{ mole} \times 273 \text{ K}} = R$$

$$8.3143 \frac{\text{N} \cdot \text{m}}{\text{mole K}} = R$$

[  $1 \text{ N} \cdot \text{m} = 1 \text{ J}$  ]

$$8.3143 \frac{\text{J}}{\text{mole K}} = R$$

$$8.3143 \frac{\text{cal}}{\text{mole K}} = R = 1.987 \text{ cal K}^{-1} \text{ mole}^{-1}$$

Thus units of "R" are expressed in energy (J) per K, per mole



## EQUATION

### MODIFICATIONS FOR MOLECULAR WEIGHT

The general gas equation can be used to calculate molecular weight of an unknown gas (the modifications are given below)

$$PV = nRT$$
$$PV = \frac{W}{M} RT$$
$$\text{or } M = \frac{WRT}{PV} \quad \text{--- (2)}$$
$$n = \frac{\text{wt of subst. (g)}}{\text{Molecular wt}}$$

Equation (2) can be used to calculate  $M$  of a gas.

### DENSITY OF GAS

Equation (1) can also be modified to calculate density of a ~~unknown~~ gas as follows

$$PV = nRT \quad \text{or} \quad PV = \frac{W}{M} RT$$
$$PV \times M = WRT$$
$$P \times M = \frac{W}{V} RT$$
$$P \times M = dRT$$
$$\frac{P \times M}{RT} = d \quad \text{--- (3)}$$
$$W = \text{wt of substance in g}$$
$$d = \frac{\text{wt of substance in g}}{\text{Volume}}$$

It must be kept in mind that general gas equation is obeyed by an ideal gas (perfect gas). A gas which obeys all gas laws under all conditions of temp & pressure. There is no ideal gas. Real gases do not obey general gas equation rigidly. However, at sufficiently high temperatures (above B.P.) the real gases start obeying gas laws. Real gases  $N_2$ ,  $H_2$ ,  $O_2$ ,  $He$  having very low B.P. almost ideally at room temperature.

## WRITE A NOTE ON ABSOLUTE ZERO.

The hypothetical temperature at which volume of a gas is reduced to zero is called Absolute Zero. It is equal to  $-273.15^{\circ}\text{C}$ . The scale of temp at which  $-273.15^{\circ}$  is taken as zero is called Absolute Temp Scale or Kelvin Scale.

In order to understand absolute zero let us consider quantitative definition of Charles' law. According to Charles' law, "Volume of a given mass of a gas increases or decreases  $\frac{1}{273}$  times its volume at  $0^{\circ}\text{C}$  by every degree rise or fall of temperature."

Let us consider a gas at  $0^{\circ}\text{C}$ . Its volume is  $V^{\circ}$ . Then according to Charles' law its

$$\text{Volume at } 1^{\circ}\text{C} = V^{\circ} + \frac{1}{273} \times V^{\circ}$$

$$\text{Volume at } -1^{\circ}\text{C} = V^{\circ} - \frac{1}{273} \times V^{\circ}$$

$$\text{Volume at } -2^{\circ}\text{C} = V^{\circ} - \frac{2}{273} \times V^{\circ}$$

$$\text{Volume at } -100^{\circ}\text{C} = V^{\circ} - \frac{100}{273} \times V^{\circ}$$

$$\text{Volume of gas at } -273^{\circ}\text{C} = V^{\circ} - \frac{273}{273} V^{\circ}$$

$$= V^{\circ} - V^{\circ} = \text{ZERO}$$

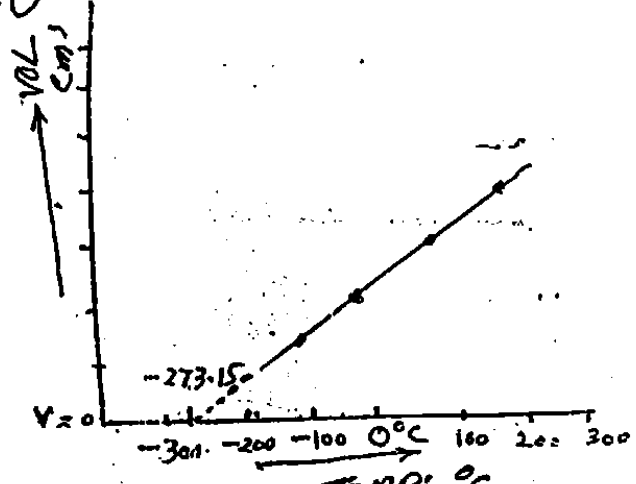
Thus according to quantitative definition of Charles' law volume of a gas is reduced to zero at  $-273^{\circ}\text{C}$ . This temp. is called Absolute Zero.

GRAPHICAL EXPLANATION: One mole of a gas at  $0^{\circ}\text{C}$  and 1 atm pressure has volume of  $22.4\text{dm}^3$ . If we plot a graph between temp. ( $^{\circ}\text{C}$ ) along x-axis and Volume along y-axis, we get a straight line. This straight line cuts x-axis at  $-273.15^{\circ}\text{C}$ .

This is possible only if we extrapolate graph upto  $-273.15^{\circ}$ . This is lowest possible temp. which can be achieved if gas the substance remains in gaseous state

Actually all gases change into liquids or solids before reaching this temp.

Charles' law is obeyed when temperature is taken on Kelvin scale



If graph between "T" and volume are plotted for different amounts of gases, different straight lines are obtained. The slopes of line is greater for larger quantity of gas. However when these lines are extrapolated, they meet at a single point ( $-273.15^{\circ}$ ) or 0 K. It is apparent that this temp. will be attained when volume of gas becomes zero. But for real gas zero volume is not possible. This temp.  $-273.15^{\circ}$  cannot be attained for real gas. Thus we can say that  $-273.15^{\circ}$  must be the coldest temperature.

WHY KELVIN SCALE HAS BEEN DEVELOPED? Charles' law is not obeyed when temperature is measured on  $^{\circ}$ C scale.

In order to understand the need of Kelvin scale let us consider a definite mass of gas at  $0^{\circ}$  having a volume of  $546 \text{ cm}^3$ . Now according to Charles' law vol of gas at  $1^{\circ}$  =  $V^{\circ} + \frac{1}{273} \times V^{\circ}$

$$= 546 + \frac{1}{273} \times 546$$

$$= 548 \text{ cm}^3$$

$$\text{Volume at } 10^{\circ} \text{C} = 546 + \frac{10}{273} \times 546 = 566 \text{ cm}^3$$

$$\text{Volume of gas at } 100^{\circ}\text{C} = 546 + \frac{100}{273} \times 546$$

$$= 746 \text{ cm}^3$$

Say  $T_1 = 10^{\circ}\text{C}$   
 $V_1 = 566$

$T_2 = 100^{\circ}\text{C}$   
 $V_2 = 746 \text{ cm}^3$

According to Charles' law

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

But in this case:  $\frac{566}{10} \neq \frac{746}{100}$

The two ratios are not equal. Hence Charles law is not obeyed if temp. is taken on  $^{\circ}\text{C}$ . For this reason a new scale has been developed at which  $-273.15^{\circ}\text{C}$  is taken as zero. This is called Kelvin scale.

If same ratio is considered at Kelvin scale the ratio remains constant

$T_1 = 10 + 273 = 283 \text{ K}$   
 $V_1 = 566 \text{ cm}^3$

$T_2 = 100 + 273 = 373 \text{ K}$   
 $V_2 = 746 \text{ cm}^3$

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

$$\frac{566}{283} = \frac{746}{373} = \text{K}$$

Hence temperature is always taken on Kelvin Scale.

# DALTONS LAW OF PARTIAL PRESSURES.

This law can be defined as, "The total pressure of a mixture of gases is equal to sum of partial pressures of individual components."

$$P_T = P_1 + P_2 + P_3 \quad \text{--- (1)}$$

$P_T$  is total pressure of mixture of gases and  $P_1, P_2, P_3$  are partial pressures of gases 1, 2, 3.

Let us consider four cylinders of same volume. Three gases  $H_2, CH_4$ , and  $O_2$  are separately enclosed in each of them at same temp. The respective pressure are 500 torr, 400 torr and 100 torr.

These gases are transferred to fourth cylinder at same temp. According to Dalton's law

$$P_T = P_{H_2} + P_{CH_4} + P_{O_2} = 1000 \text{ Torr}$$
$$P_T = 500 + 400 + 100 \text{ Torr}$$

These three are non reacting gases. The molecules are moving independently. They have equal chance of collision on walls of container. Thus each gas exerts its own pressure in mixture. The total pressure is the result of total number of collisions per unit area per unit time.

Let us apply general gas equation to individual gases in the mixture

$$P_{H_2} V = n_{H_2} RT \quad \text{OR} \quad P_{H_2} = \frac{n_{H_2} RT}{V} \Rightarrow P_{H_2} \propto n_{H_2}$$

$$P_{CH_4} V = n_{CH_4} RT \Rightarrow P_{CH_4} = \frac{n_{CH_4} RT}{V} \quad P_{CH_4} \propto n_{CH_4}$$

$$P_{O_2} V = n_{O_2} RT \Rightarrow P_{O_2} = \frac{n_{O_2} RT}{V} \quad P_{O_2} \propto n_{O_2}$$

The "T" and "V" are same. Volume each gas in mixture. Thus the value  $\frac{RT}{V}$  is constant. Partial pressure of

gas is directly proportional to number of moles of gas

$$P_t = P_{H_2} + P_{CH_4} + P_{O_2} \quad \text{--- (2)}$$

$$P_t = n_{H_2} \frac{RT}{V} + n_{CH_4} \frac{RT}{V} + n_{O_2} \frac{RT}{V} \quad \text{--- (3)}$$

$$P_t = (n_{H_2} + n_{CH_4} + n_{O_2}) \frac{RT}{V}$$

$$P_t = n_t \frac{RT}{V}$$

$$P_t V = n_t RT \quad \text{--- (4)}$$

### CALCULATION OF PARTIAL PRESSURE OF EACH GAS.

The partial pressure of each gas can be calculated if we know moles of each gas and total no. of moles in the mixture.

Let us consider two gases "A" and "B" in a cylinder. Their number of moles are  $n_A$  and  $n_B$  respectively. Then writing general gas eq. for each gas

$$P_A V = n_A RT \quad \text{--- (5)}$$

$$P_B V = n_B RT \quad \text{--- (6)}$$

For mixture  $P_t V = n_t RT \quad \text{--- (7)}$

Dividing eq. (5) and (6) by eq. (7) we get

$$\frac{P_A V}{P_t V} = \frac{n_A RT}{n_t RT} \quad \text{--- (8)}$$

$$\frac{P_B V}{P_t V} = \frac{n_B RT}{n_t RT} \quad \text{--- (9)}$$

$$\frac{P_A}{P_t} = \frac{n_A}{n_t} \quad \text{--- (10)}$$

$$\frac{P_B}{P_t} = \frac{n_B}{n_t} \quad \text{--- (11)}$$

$$P_A = \frac{n_A}{n_t} P_t \quad \text{--- (12)}$$

$$P_B = \frac{n_B}{n_t} P_t \quad \text{--- (13)}$$

$$P_A = X_A P_t \quad \text{--- (14)}$$

$$P_B = X_B P_t \quad \text{--- (15)}$$

" $X_A$ " and " $X_B$ " are called mole fractions of gas "A" and "B" respectively.

APPLICATIONS OF DALTONS LAW

CORRECTION OF GASES OVER WATER

Gases which are insoluble in water are collected over water in lab. Whenever a gas is collected over water, some vapours are also included in gas. This is called wet gas. The total pressure is  $P_T = P_{gas} + P_{vapours}$ . In order to get pressure of dry gas, pressure of vapours must be subtracted from total pressure.

$$P_T - P_{vap.} = P_{dry\ gas}$$

Pressure of vapours is called aqueous tension.

RESPIRATION PROCESS / The respiratory pressure depends upon difference in partial pressures of gases.

The partial pressure of  $O_2$  is greater in inhaled Air. The partial pressure of  $O_2$  is lesser in blood supplied to the lungs. Thus oxygen diffuses from Air to blood.

The partial pressure of  $CO_2$  is greater in blood and lesser in Air. Thus  $CO_2$  diffuses out.

BREATHING AT HIGH ALTITUDES / At high altitudes, partial pressure of oxygen is decreased (below  $159\ g/cm^3$ ). Thus pilots feel uncomfortable breathing in their unpressurized cabins.

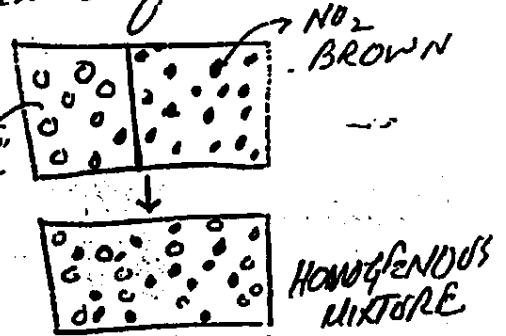
DEEP SEA DIVING / Deep sea divers take 4%  $O_2$  mixed with an inert gas "He" in their tank and adjust pressure of  $O_2$  according to requirement.

# DIFFUSION OF GASES

The intermixing of gases in all proportions to form a homogeneous mixture called diffusion. Gas diffusion is due to constant motion of gas molecules in random directions and their collisions with one another and also with walls of container.

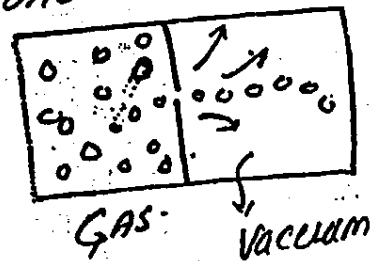
EXAMPLES: Spreading of fragrance of rose or scent when two gases diffuse, they try to make their partial pressures same every where.

Suppose  $\text{NO}_2$  a brown gas and  $\text{O}_2$  a colourless gas are separated from each other by a partition when partition is removed, both diffuse into each other due to collision and random motion. A stage is reached when gases generally a homogeneous mixture. The pressure becomes uniform every where.



## EFFUSION

The escape of gas molecules from aperture of very small size one by one without collision is called effusion. It is spreading is not due to collision but their tendency to escape one by one. Molecules constantly collide with walls of container. When a molecule approaches the wall in front of opening it enters the other portion of vessel. This is called effusion.





# GRAHMS LAW OF DIFFUSION AND EFFUSION 17

It states that "the rate of diffusion or effusion of a gas is inversely proportional to square root of its density at constant temperature and pressure."

According to Graham's law Rate of diffusion  $\propto \frac{1}{\sqrt{d}}$  (at const T, P)

$$\text{Rate of diffusion} = \frac{k}{\sqrt{d}}$$

$$\text{Rate of diffusion} \times \sqrt{d} = k$$

$$\text{Rate} \times \sqrt{d} = k$$

k is constant for all gases at same temp. and pressure. Let us consider two gases "1" and "2" their respective rates of diffusion and densities are  $r_1, r_2, d_1, d_2$

Then according to Graham's law

$$r_1 \propto \frac{1}{\sqrt{d_1}}$$

and

$$r_2 \propto \frac{1}{\sqrt{d_2}}$$

$$r_1 = k \frac{1}{\sqrt{d_1}}$$

$$r_2 = k \frac{1}{\sqrt{d_2}}$$

$$r_2 \times \sqrt{d_2} = k$$

$$r_1 \times \sqrt{d_1} = k$$

Then by dividing above two equations

$$\frac{r_1 \sqrt{d_1}}{r_2 \sqrt{d_2}} = \frac{k}{k}$$

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

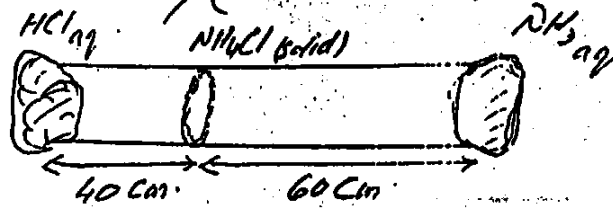
Since densities are proportional to molecular masses so Graham's law can also be written as

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}} \text{ (at Constant T, P)}$$

## EXPERIMENTAL VERIFICATION:-

Take a 100 cm long glass tube. It is opened at both ends. Put a cotton plug soaked in ammonia in one end and cotton plug soaked in HCl in other end simultaneously (at a time).

The vapours of both gases are colourless (invisible) but when these vapours meet, they produce a white dense fumes of  $NH_4Cl$  (solid).



The two gases are found to escape from respective plugs and react to produce  $NH_4Cl$ . The  $NH_4Cl$  produced is 60 cm away from  $NH_3$  and 40 cm away from HCl. The ratio of velocities of two gases depend upon distance covered by these vapours.

$$\frac{v_{NH_3}}{v_{HCl}} = \frac{\text{Distance covered by } NH_3}{\text{Distance covered by } HCl}$$

$$\frac{v_{NH_3}}{v_{HCl}} = \frac{60}{40} = 1.5$$

$$\text{OR } \frac{r_{NH_3}}{r_{HCl}} = 1.5$$

This ratio indicates relative rate of diffusion of two gases. This relative rate of diffusion has been determined experimentally. Now let us apply Graham's Law to calculate relative rates of diffusion.

According to Graham's Law:-

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{\text{density of HCl}}{\text{density of } NH_3}} \quad \text{OR} \quad \frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{1.66}{0.76}}$$

$$\left. \begin{aligned} \text{density of HCl} &= 1.66 \text{ g/dm}^3 \\ \text{density of } NH_3 &= 0.76 \text{ g/dm}^3 \end{aligned} \right\}$$

$$\frac{r_{NH_3}}{r_{HCl}} = 1.5$$

This is equal to ratio calculated experimentally.

$$\text{Similarly } \frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{\text{M.O.T of HCl}}{\text{M.O.T of } NH_3}}$$

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{36.5}{17}}$$

$$\frac{r_{NH_3}}{r_{HCl}} = 1.465$$

$$\frac{r_{NH_3}}{r_{HCl}} \approx 1.5$$

These results verify Graham's Law.

# KINETIC THEORY OF GASES:

In order to explain behaviour of gases quantitatively Bernoulli put forward kinetic molecular theory of gases. Clausius derived kinetic equation from this theory and deduced all gas laws from it. The theory was further explained by Maxwell. He gave law of distribution of molecular velocities. According to this law there are groups of molecules having definite velocity range. Boltzmann studied distribution of energies among gas molecules. Fundamental postulates of K.T.G are given below

## Q. POSTULATES OF K.T.G. & DERIVATION OF GAS LAWS ON THE BASIS OF K.T.G.

The main postulates of K.T.G. are given below.

- 1) All gases consist of very small particles called atoms or molecules. (atoms for monoatomic gases only eg He, Ne)
- 2) The actual size of gas molecule is negligible as compared to total volume of gas. So most of space in a gas container is empty.
- 3) There are no forces of attraction or repulsion between gas molecules. Thus each molecule moves independently.
- 4) The gas molecules are constantly moving in straight line. Their direction changes when they collide with another molecule or with walls of container.
- 5) Due to their motion gas molecules possess K.E. The temperature of gas is measure of average kinetic energy of gas molecules. The average speed and average kinetic energy is directly proportional to temp. on Kelvin Scale.
- 6) At same temperature different gases have same average K.E.
- 7) Gas molecules are constantly moving in random directions. Their direction changes only when they collide with another molecule or walls of container. Pressure of gas is due to collisions of molecules on walls of container.
- 8) Force of gravity has no influence on gas molecules.
- 9) The collision of molecules is elastic i.e they do not lose any kinetic energy on collision. The collision without any gain or loss of energy is called Elastic Collision.

9mp.

# WHAT IS KINETIC EQUATION? DERIVE GAS LAWS FROM K.T.G; USING KINETIC EQUATION?

By using kinetic theory of gases R.J. Clausius deduced an expression for the pressure of an ideal gas. According to K.T.G, gas molecules are constantly moving they collide with one another and also with walls of container. Due to these collisions they exert some force on walls of container. This force per unit area exerted by gas molecules is called pressure. The kinetic eq. derived by Clausius is  $PV = \frac{1}{3} mn \bar{c}^2$  — (1)

$P$  = Pressure,  $V$  = volume,  $m$  = mass of one molecule  
 $n$  = number of molecules,  $\bar{c}^2$  = mean sq. velocity.

All gas molecules do not have same velocities. If there are " $n_1$ " molecules with velocity " $c_1$ " and " $n_2$ " molecules with velocity " $c_2$ " then

$$\bar{c}^2 = \frac{n_1 c_1^2 + n_2 c_2^2 + n_3 c_3^2 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$\bar{c}^2$  is called average of sq. of velocities i.e. mean sq. velocity

The sq. root of mean sq. velocity is called  $C_{rms}$ .

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

This equation is quantitative relationship between the absolute temperature and velocities of gas molecules. According to this equation higher the temperature of gas greater is the velocity of molecules.

## EXPLANATION OF GAS LAWS FROM KINETIC EQ.

BOYLE'S LAW: According to Boyle's law volume of a given mass of gas is inversely proportional to pressure at constant temperature.  $V \propto \frac{1}{P}$  at const  $T$

$v = k \times \frac{1}{P}$  or  $P \times v = k$  — (1)

According to K.T.G the kinetic energy of molecules is directly proportional to absolute temperature.

$\frac{1}{2} m n \bar{c}^2 \propto T$

$\frac{1}{2} m n \bar{c}^2 = kT$  — (2)

According to kinetic equation:  
Multiplying and dividing by 2

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

$PV = \left(\frac{1}{3} m n \bar{c}^2\right) \times \frac{2}{2}$

$PV = \left(\frac{1}{2} m n \bar{c}^2\right) \frac{2}{3}$

Since  $\frac{1}{2} m n \bar{c}^2 = kT$

$PV = kT \frac{2}{3}$  — (3)

At constant "T" R.H.S of eq. (3) is constant  
 $PV = \text{Constant}$  — (4)

Thus product of pressure and volume remains constant at constant temperature. This is Boyle's Law.

CHARLES' LAW:

According to Charles' Law volume of a given mass of gas is directly proportional to absolute Temp. at constant pressure.

$V \propto T$

$V = kT$  — (5) "k" is constant

$\frac{V}{T} = k$  — (6)

Eq. (6) can be defined as "Ratio of volume and Temp. always remains constant at constant pressure"

From eq. (3)  $PV = kT \frac{2}{3}$

$V = kT \frac{2}{3P}$

$V = \frac{2}{3P} kT$

At constant pressure  $\frac{2}{3P} k = k'$

$V = k' T$  or  $V \propto T$

$\frac{V}{T} = k'$  — (7)

Equation 7 is mathematical form of Charles' Law.

AVOGADRO'S LAW:

According to this law equal volumes of different gases under same conditions of temp and pressure contain equal no. of molecules.

Let us consider two gases 1 and 2 at same pressure & volume. The number of molecules are  $n_1$  and  $n_2$  respectively.

The kinetic equation for these two gases could be written as

$$PV = \frac{1}{3} m_1 n_1 \bar{c}_1^2 \quad \text{--- (1)}$$

$$PV = \frac{1}{3} m_2 n_2 \bar{c}_2^2 \quad \text{--- (2)}$$

Since L.H.S of these two equations is equal. Thus R.H.S. are also equal

$$\frac{1}{3} m_1 n_1 \bar{c}_1^2 = \frac{1}{3} m_2 n_2 \bar{c}_2^2$$

$$m_1 n_1 \bar{c}_1^2 = m_2 n_2 \bar{c}_2^2 \quad \text{--- (3)}$$

At same temp. mean average K.E. of molecule will be the same

$$\frac{1}{2} m_1 \bar{c}_1^2 = \frac{1}{2} m_2 \bar{c}_2^2 \quad \text{--- (4)}$$

Dividing eq. (3) by eq. (4) we get

$$\frac{m_1 n_1 \bar{c}_1^2}{m_1 \bar{c}_1^2} = \frac{m_2 n_2 \bar{c}_2^2}{m_2 \bar{c}_2^2}$$

$$n_1 = n_2 \quad \text{--- (5)}$$

That's equal volume of all gases at same conditions of temp and pressure will have equal number of molecules. This is Avogadro's Law.

GRAHMS LAW OF DIFFUSION: According to Graham's Law  $r \propto \frac{1}{\sqrt{M}}$  at constant temperature and pressure.

Kinetic equation for volume of gas could be written as

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

For 1 mol of gas containing Avogadro's number of molecules

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

( $m N_A =$  Molecules wt of compound)

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

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

Taking sq. root of both sides

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

$$\sqrt{\frac{3P}{M/d}} = \sqrt{\bar{c}^2}$$

$$\sqrt{\frac{3P}{d}} = \bar{c}$$

At constant pressure  $\sqrt{\frac{1}{d}} \propto \bar{c}$  which is Graham's law.  
 ( $\bar{c}$  = rate of diffusion)

$$\sqrt{\frac{1}{d}} \propto r$$

KINETIC INTERPRETATION OF TEMPERATURE.

According to kinetic equation pressure of gas is due to collision of gas molecules on walls of container. The kinetic equation could be written as  $PV = \frac{1}{3} m n \bar{c}^2$  — (1)  
 The kinetic energy is due to translational motion of molecule. It is given by following expression  $E_k = \frac{1}{2} m \bar{c}^2$  — (2)  
 $E_k$  is average translational K.E. of gas molecule.

Multiplying and kinetic eq by (2) we get

$$PV = \left(\frac{1}{3} m n \bar{c}^2\right) \times \frac{2}{2}$$

$$PV = \left(\frac{1}{2} m \bar{c}^2\right) \frac{2}{3} n$$
 — (3)

Putting value of  $\frac{1}{2} m \bar{c}^2$  in eq 3 from eq 2.

$$PV = E_k \frac{2}{3} n$$

$$\frac{3PV}{2n} = E_k$$
 — (4)

For 1 mole of gas  $n = "N_A"$  (1 mole of contains Avogadro's no. of molecules)

$$\frac{3}{2} \frac{PV}{N_A} = E_k$$

$$\frac{3}{2} \frac{R}{N_A} T = E_k$$
 — (5)

( $PV = RT$  for 1 mole of gas)

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According to eq (5) kelvin temp. is directly proportional to average translational kinetic energy of molecules.  
Thus change in temp. means change in translational K.E.

FLOW OF HEAT When heat flows from one body to another, the molecules of hotter body give some of their <sup>kinetic</sup> energy to molecules of colder body by collisions. This process goes on until translational K.E. of all molecules becomes equal and temp. also becomes equal.

TEMPERATURE OF SOLIDS In gases and liquids temperature is measure of average K.E. of molecules. In solids molecules cannot have translational K.E., temperature is measure of vibrational K.E.

ABSOLUTE ZERO According to kinetic interpretation of temperature, absolute zero is that temperature at which the molecular motion will stop. The absolute zero is unattainable. The temp. as low as  $10^{-5}$  K. has been attained.

LIQUEFACTION OF GASES:

GENERAL PRINCIPLE: - The gases can be converted into liquids by two methods  
(i) By application of pressure  
(ii) By decreasing temperature.

At high pressure molecules get closer to each other and develop some forces of attraction among themselves. At low temp. the K.E. of molecules is decreased and attractive forces become dominant.

CRITICAL TEMPERATURE The temperature beyond which no gas can be liquified by application of pressure and below which continuous increase in pressure



brings about liquifaction is called CRITICAL TEMP. For example  $\text{CO}_2$  cannot be converted into liquid by application of pressure if its temp. is above  $31^\circ\text{C}$ . However if temp. is below  $31^\circ\text{C}$ , increase in pressure will change  $\text{CO}_2$  into liquid. Thus  $31^\circ\text{C}$  is critical temp. of  $\text{CO}_2$ .

In other words critical temp. is the highest temp. at which a substance can exist as a liquid. Beyond which liquid form is not possible.

CRITICAL PRESSURE " $P_c$ " The pressure required to convert a gas into liquid at critical temp. " $T_c$ " is called CRITICAL PRESSURE " $P_c$ ".

FACTORS AFFECTING CRITICAL TEMPERATURE

The value of critical temp. of gas depends upon

1) SIZE OF MOLECULES

(2) SHAPE OF MOLECULE

3) INTER MOLECULAR FORCES.

Non polar gases with low polarizability, have low critical temp. while polar gases like  $\text{H}_2\text{O}$ ,  $\text{NH}_3$  have high critical temp. i.e they have better ability to change into liquid.

IMPORTANCE The knowledge of critical temp. and critical pressure provide us information about conditions under which a gas can change into liquid. For example  $\text{O}_2$  has critical temp.  $154.4\text{K}$  ( $-118.75^\circ\text{C}$ ). It means it must be cooled below this temperature to convert it into liquid by application of pressure. Ammonia is a polar gas with critical temp  $405.6\text{K}$  ( $132.44^\circ\text{C}$ ). It indicates that  $\text{NH}_3$  can be easily liquified by application of pressure near room temperature.

Please. See Table 3.2 (Page 78)

## METHODS OF LIQUEFACTION OF GASES.

### JOULE THOMSON EFFECT:

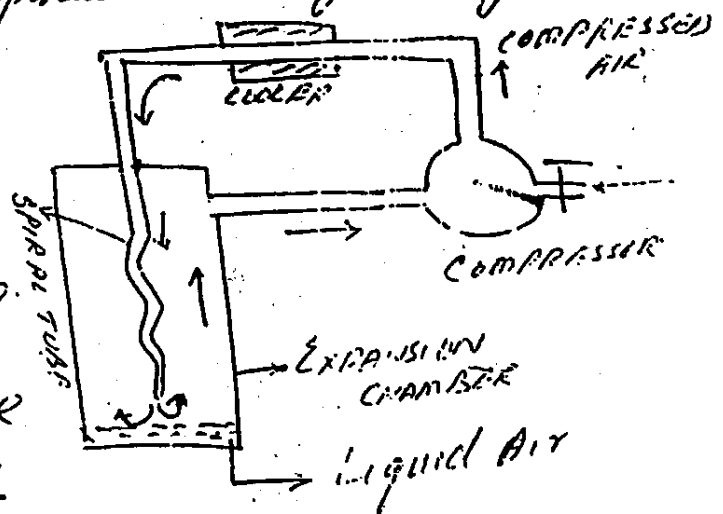
**PRINCIPLE:** When a highly compressed gas is allowed to expand into a region of low pressure cooling takes place.

When a gas is compressed, molecules get closer to each other and develop some forces of attraction among themselves. When gas is allowed to expand suddenly, the molecules move apart from each other. They have to break intermolecular force. The energy required for this purpose is absorbed from the gas itself. Thus gas is cooled.

### LINDS' METHOD OF LIQUEFACTION OF GASES:

**PRINCIPLE:** It is based upon Joule Thomson effect i.e. when a highly compressed gas is allowed to expand cooling takes place. The apparatus used for this purpose is shown below.

The air is compressed to about 200 atm. Then it is passed through cooler to remove heat of compression. It is then allowed to pass through a spiral pipe having a jet at the end.



The air is allowed to expand from 200 atm to 1 atm. Cooling takes place due to expansion. The cooled air goes upward and cools incoming compressed air. Then it is returned to compressor pump. The process is repeated over and over again. The liquid air is collected at the bottom of chamber.

All gases except  $H_2$  and  $He$  can be liquefied by this procedure.

# REAL GASES

## "NON IDEAL BEHAVIOUR" OF REAL GASES

Q: WHAT ARE IDEAL AND NON IDEAL GASES? WHY DO REAL GASES DEVIATE FROM IDEAL BEHAVIOUR?

ANS: IDEAL GAS:-

A gas which obeys Boyle's law and Charles' law under all conditions of temperature and pressure is called AN IDEAL GAS. There is no perfectly ideal gas. For example according to Boyle's law,

The product of pressure and volume should remain constant at constant temperature.  $PV = K$  (at const. Temp.)

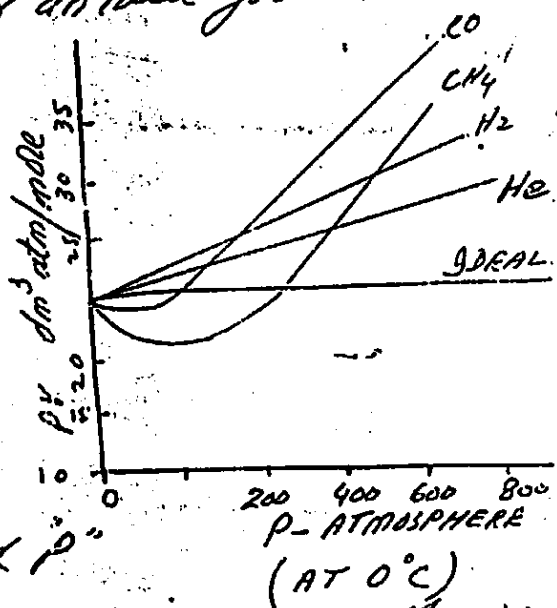
With increase or decrease in pressure there should be proportionate decrease or increase in volume.

Thus if a graph is plotted between "P" (along x-axis) and "PV" on y-axis, a horizontal line parallel to x-axis should be obtained for an ideal gas. (As shown below)

REAL GASES The real gases like  $H_2$ ,  $N_2$ ,  $O_2$ ,  $CO_2$  etc. do not obey gas laws at all conditions of temp. and pressure.

These gases show marked deviations from ideal behaviour. The magnitude and nature of deviation depend upon nature of gas and conditions of "T" and "P".

The deviation for  $H_2$ , He,  $CO_2$ ,  $CH_4$  at  $0^\circ C$  are shown in graph. The deviations from ideality are much more pronounced at (i) LOW TEMPERATURE (ii) AT HIGH PRESSURE.



When same gases are studied or experimentally at higher temperature (say  $100^\circ C$ ) the deviations become less serious.

## CAUSES OF DEVIATION:

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The real gases deviate from ideal behaviour due to two faulty assumptions in kinetic theory of gases.

1. The actual size of gas molecule is negligible as compared to total volume occupied by gas.
2. There are no forces of attraction or repulsion between gas molecules and each gas molecule behaves independently.

The deviations from ideality depend upon following factors.

- (i) Nature of gas (ii) Temperature (iii) Pressure.
- The deviations are much more pronounced at low temp. and high pressure. The first assumption is responsible for deviation at high pressure and second postulate is responsible for deviation at low temperature.

**DEVIATION AT HIGH PRESSURE:** At high pressure the gas molecules come closer to each other. The empty spaces between molecules decrease. Thus actual volume occupied by gas molecule is not negligible at this state, as compared to total volume of gas. Further when gas molecules come closer to each other they do have some forces of attraction for each other.

**DEVIATION AT LOW TEMPERATURE:** When temperature is very high, kinetic energy of molecules is very large.

The forces of attraction between them are negligible. However at low temperature kinetic energy becomes very low. The intermolecular forces remain no more negligible. This collision between molecules are not elastic at low temp. Therefore gases show marked deviations at low temperature.

Non-polar gases and monoatomic gases such as  $H_2$  have very low B.P. ( $-252.7^\circ C$  for  $H_2$ ) behave almost ideally at room temperature because room temperature ( $25^\circ C$ ) is sufficiently high temperature for these gases. On the other hand polar gases like  $SO_2$ ,  $H_2S$  with relatively high B.P. show more deviations at room temperature. Because polar gases do have some intermolecular forces (dipole-dipole interactions) at room temperature.

# VANDER WAALS EQUATION FOR REAL GASES

The real gases show deviations from ideal gas equation ( $Pr = nRT$ ). Vander Waals pointed out that both pressure and volume factors in ideal gas equation must be corrected. Then the real gases will obey that equation called Vander Waals equation. Let us derive this equation

VOLUME CORRECTION: When a gas is compressed by application of pressure, the gas molecules get closer to each other. With increase in pressure volume of gas goes on decreasing. Ultimately a stage is reached when no more decrease in volume is possible with increase in pressure. This is due to definite size of gas molecule. At low pressure this actual size is almost negligible. But at high pressure this actual size can not be neglected. The volume available to gas molecules is

$$V_{free} = V - b \quad \text{--- (1)}$$

$V$  = volume of container

$b$  = effective volume of molecules per mole of gas

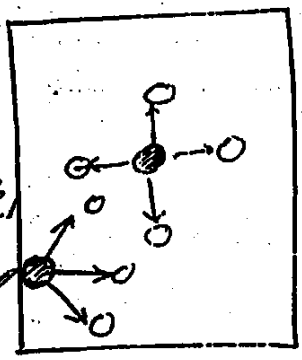
" $b$ " is called excluded volume which is characteristic of each gas. Its value depends upon size of gas molecules. The excluded volume is four times the actual volume of gas molecule

$$b = 4V_m \quad \text{--- (2)}$$

" $V_m$ " is actual volume of 1 mole of gas molecules. Thus Vander Waals pointed out that the term " $V$ " in ideal gas equation must be replaced by ( $V_{free} = V - b$ ) to make it applicable to real gases. For ideal gases actual volume is equal to zero. Thus  $V_{free} = V$  i.e. volume of container is equal to  $V_{free}$ .

# PRESSURE CORRECTION: <sup>30</sup>

Let us consider a gas molecule in the centre of container. It is surrounded by other gas molecules in all directions. Thus net attractive force on molecule is zero. But when molecule is very close to walls of container, it is slightly pulled backward by other molecules. Thus force of collision is decreased.



Thus pressure exerted by real gas molecules on walls of container will be less than that of ideal gas pressure. Thus observed pressure on walls is less than  $P_{ideal}$  by a factor  $P'$ .

$$P = P_i - P' \quad (P' = \text{Pressure used to overcome forces of attraction})$$

$$P + P' = P_i \quad \text{--- (3)}$$

Thus true kinetic pressure which molecules would have exerted in absence of forces of attraction is  $P_i = P + P'$ . The ' $P'$ ' decreases with increase in volume of gas because molecules move apart and forces of attraction are decreased.

The pressure used to overcome forces of attraction is given by  $P' = \frac{a}{V^2}$  --- (4).  $a$  is called coefficient of attraction per unit vol. It depends upon nature of gas. Thus effective kinetic pressure  $P_i = P + \frac{a}{V^2}$  --- (5).

Putting value of  $V_{free}$  and ' $P_i$ ' in eq  $PV = RT$  for one mole of gas we get

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{--- (6)}$$

For ' $n$ ' moles of gas it could be written as

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad \text{--- (7)}$$

"a" and "b" are called Vander Waal's constants<sup>31</sup>  
"a" is expressed in  $\text{atm dm}^3/\text{mole}^2$  and "b" is expressed in  $\text{dm}^3/\text{mole}$

In SI system units of  $a = \text{Nm}^4/\text{mole}^2$

$b = \text{m}^3/\text{mole}$

The values of a, b can be determined by knowing values of P, V, T under two different conditions. ✓

The greater the intermolecular forces greater is the "a" factor.

### PLASMA STATE:

The state in which many of the atoms or ions molecules are effectively ionized and it allows the charges to flow freely is called plasma state. It is known as fourth state of matter. Since 99% of the known universe is in plasma state and it has been formed since BIG BANG, plasma might be considered as first state of matter. Plasma is a conductor of electricity, and it has a unique physics as compared to solids, liquids & gas.

### FORMATION OF PLASMA

When a solid is heated, the thermal energy increases and it changes into liquid. This is called phase transition. This process takes place at a constant temp. and pressure. The amount of heat required is called latent heat of fusion. When a liquid is heated K.E. of molecules increases and ultimately it changes into gas. It is also phase transition. The amount of heat required for this conversion is called latent heat of vaporization. It takes place at const. Temp. called boiling point. However when a gas is heated, first molecules change into atoms. At with increase in temp. these atoms get ionized due to removal of outermost electrons. The resulting substance is

a mixture of neutral atoms, positively charged ions and negatively charged electrons. This mixture is called PLASMA. The transition from gas to an ionized gas (plasma) form is not a phase transition. It occurs gradually with increasing temp.

CHARACTERISTICS OF PLASMA | Since all particles are electrically charged they are able to interact with electromagnetic field - many phenomena not present in ordinary solids and liquids can be found in plasma.

The free electrons in metals can also be considered as plasma.

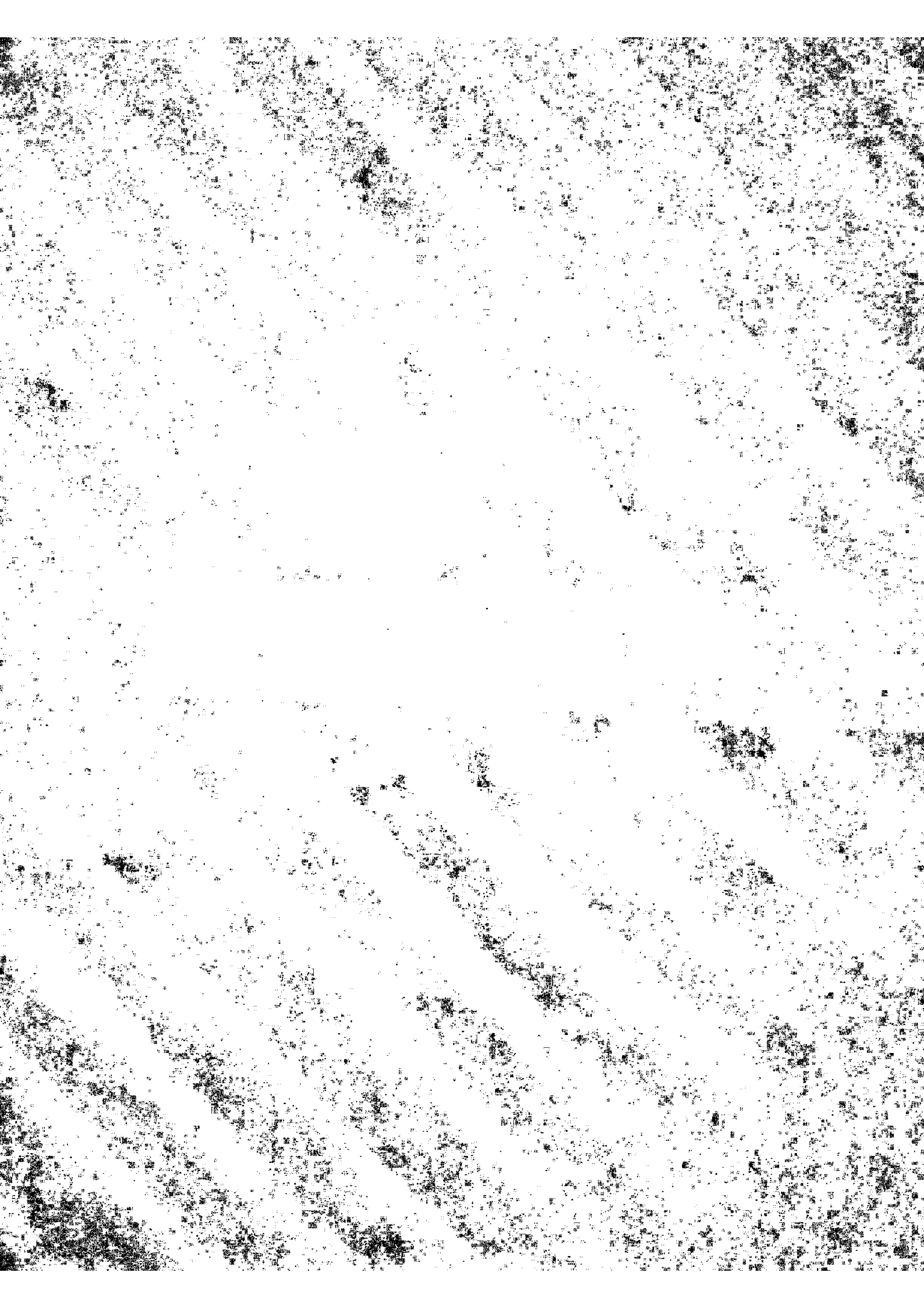
Most of universe consist of matter in plasma state. The ionization in matter is caused by heat or radiations.

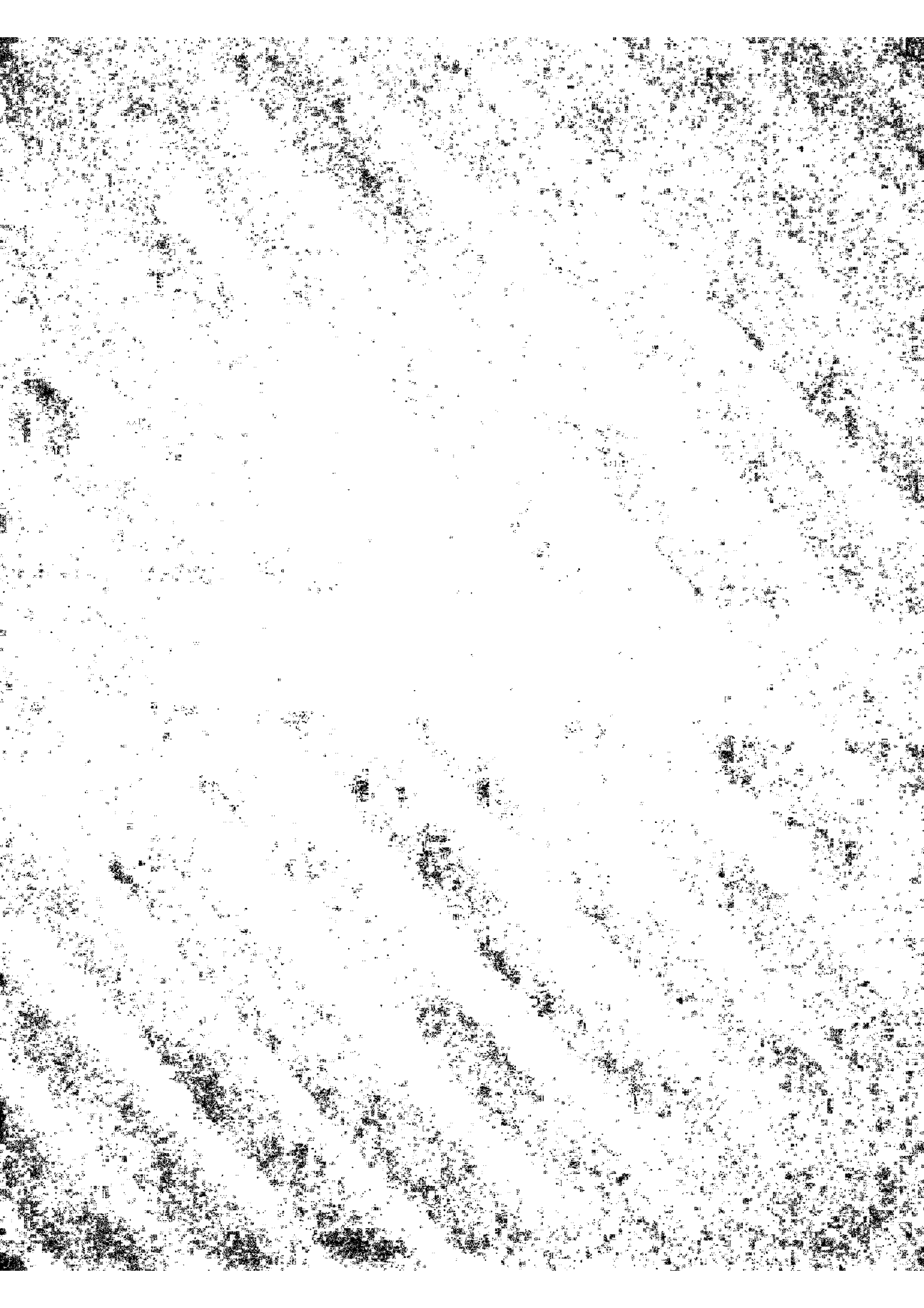
Thus plasma is the substance in which many of atoms or molecules are effectively ionized and it allows flow of charges.

### APPLICATIONS OF PLASMA

1. In every fluorescent lamp there is present plasma. Plasma converts electric power to a form which strikes phosphor coating of lamp and produces light. Phosphor is a white coating on walls of bulb.
  2. It is used for sterilization of food.
  3. It is used for sterilization of operation theaters.
- The plasma system kills bacteria, viruses, fungi and spores.







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Q20 Working at a vacuum line, a chemist isolated a gas in a weighing bulb with volume of 255 cm<sup>3</sup>, at a temperature of 25 °C and under a pressure in the bulb of 10.0 torr. The gas weighed 12.1 mg. What is the molecular mass of this gas?

$$V_1 = 255 \text{ cm}^3 = \frac{255}{1000} = 0.255 \text{ dm}^3$$

$$T = 25^\circ\text{C} + 273 = 298 \text{ K}$$

$$P = 10 \text{ TORR} = \frac{10}{760} = 0.0132 \text{ ATM}$$

$$\text{mass} = 12.1 \text{ mg} = \frac{12.1}{1000} = 0.0121 \text{ g}$$

$$PV = nRT$$

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

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

$$M = \frac{0.0121 \times 0.0821 \times 298}{0.0132 \times 0.255}$$

ANSWER

$$M = 88 \text{ g/MOLE}$$

Q NO. 21

Q21 What pressure is exerted by a mixture of 2.00g of H<sub>2</sub> and 8.00 g of N<sub>2</sub> at 273K in a 10 dm<sup>3</sup> vessel?

$$H_2 = 2 \text{ g} = \frac{2}{2} = 1 \text{ MOLE}$$

$$N_2 = 8 \text{ g} = \frac{8}{28} = 0.286 \text{ MOLE}$$

$$\text{TOTAL MOLES} = 1.286 \text{ MOLE}$$

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

$$V = 10 \text{ dm}^3$$

By using

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

$$P = \frac{1.286 \times 0.0821 \times 273}{10}$$

$$(P = 2.88 \text{ ATMOSPHERE})$$

Q NO. 22

Q22 (a) The relative densities of two gases A and B are 1:1.5. Find out the volume of B which will diffuse in the same time in which 150 dm<sup>3</sup> of A will diffuse?

By using GRAMM'S LAW

$$\frac{V_B}{V_A} = \sqrt{\frac{d_A}{d_B}}$$

$$\frac{V_B}{150} = \sqrt{\frac{1}{1.5}}$$

$$\frac{V_A}{V_B} = \sqrt{\frac{d_B}{d_A}} \quad \text{or} \quad \frac{V_A}{V_B} = \sqrt{\frac{1.5}{1}}$$

$$\frac{150}{V_B} = 1.224$$

$$\text{ANS } \boxed{122.54 \text{ cm}^3} = \frac{150}{1.224} = V_B$$

(b) Hydrogen ( $\text{H}_2$ ) diffuses through a porous plate at a rate of  $500 \text{ cm}^3$  per minute at  $0^\circ\text{C}$ . What is the rate of diffusion of oxygen through the same porous plate at  $0^\circ\text{C}$ ?

(b)

Rate of diffusion of  $\text{H}_2 = 500 \text{ cm}^3/\text{min.}$

Rate of diffusion of  $\text{O}_2 = ?$

According to Graham's law

$$\frac{r_{\text{H}_2}}{r_{\text{O}_2}} = \sqrt{\frac{\text{M.Wt of O}_2}{\text{M.Wt of H}_2}}$$

$$\frac{500}{r_{\text{O}_2}} = \sqrt{\frac{32}{2}}$$

$$500 \times 4 = r_{\text{O}_2}$$

4

$$\boxed{\frac{125 \text{ cm}^3}{\text{min.}} = r_{\text{O}_2}$$

(c) *can*

(c) The rate of effusion of an unknown gas A through a pinhole is found to be 0.279 times the rate of effusion of  $\text{H}_2$  gas through the same pinhole. Calculate the molecular mass of the unknown gas at STP.

Let rate of effusion of hydrogen =  $x$

Then rate of effusion of unknown gas =  $0.279x$

Molecular wt of  $\text{H}_2 = 2$

M.Wt. of unknown gas = ?

According to Graham's law

$$\frac{r_{\text{H}_2}}{r_{\text{unk}}} = \sqrt{\frac{\text{M.Wt of unknown}}{\text{M.Wt of H}_2}}$$

$$\frac{x}{0.279x} = \sqrt{\frac{\text{M.Wt of Unknown}}{\text{M.Wt of H}_2}}$$

Taking sq. of both sides

$$\frac{1}{0.0778} = \frac{\text{MWT of unknown}}{2}$$

$$\frac{2}{0.0778} = \text{MWT of unknown}$$

$$\boxed{25.7} = \text{MWT}$$

Q.No. 93

CALCULATE NO. OF MOLECULES AND NO. OF ATOMS IN FOLLOWING GASES

(a) 20 cm<sup>3</sup> OF CH<sub>4</sub> AT 0°C AND 760 mm(Hg) PRESSURE

$$V_1 = \frac{20}{1000} = 0.02 \text{ dm}^3$$

$$P = \frac{760}{760} = 0.92 \text{ ATM}$$

$$T_1 = 0 + 273 = 273 \text{ K}$$

By using GENERAL GAS EQUATION

$$PV = nRT$$

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

$$\frac{0.92 \times 0.02}{0.0821 \times 273} = n$$

$$8.21 \times 10^{-4} \text{ mole} = n$$

$$\begin{aligned} \text{NUMBER OF MOLECULES} &= \text{MOLES} \times \text{AVOGADRO'S NUMBER} \\ &= 8.21 \times 10^{-4} \times 6.022 \times 10^{23} \\ &= 4.94 \times 10^{20} \text{ MOLECULES} \end{aligned}$$

MOLECULE OF CH<sub>4</sub> CONTAINS ATOMS = 5

$$4.94 \times 10^{20} \times 5 = 2.47 \times 10^{21} \text{ ATOMS}$$

$$(b) V = 1 \text{ cm}^3 = \frac{1}{1000} = 10^{-3} \text{ dm}^3$$

$$T = 100^\circ\text{C} + 273 = 373 \text{ K}$$

$$P = 1.5 \text{ atm}$$

$$PV = nRT$$

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

$$\frac{1.5 \times 10^{-3}}{0.0821 \times 373} = n$$

$$\Rightarrow n = 4.9 \times 10^{-5} \text{ moles}$$

P-6

$$\begin{aligned} \text{NO. OF MOLECULES} &= \text{MOLES} \times \text{AVOGADRO'S NO.} \\ &= 4.9 \times 10^{-5} \times 6.022 \times 10^{23} \end{aligned}$$

$$\text{NO. OF MOLECULE OF } \text{NH}_3 = 2.89 \times 10^{19}$$

$$\text{NO. OF ATOMS} = 2.89 \times 10^{19} \times 4$$

(1 MOLECULE  
CONTAINS = 4 AT.)

$$= 1.16 \times 10^{20} \text{ ATOMS}$$

Q17 Methane gas is enclosed in a vessel having a volume of 100 cm<sup>3</sup> and at a pressure of 760 torr. It is carefully compressed at a constant temperature in successive changes of pressure i.e. 20 torr at a time, until the final pressure is 200 torr. Calculate each new volume and prepare a plot of P versus V by taking pressure on the x-axis

$$\text{MOLECULES} = 10^{20}$$

$$\text{MOLE} = \frac{\text{NO. OF MOLECULES}}{\text{AVOGADRO'S NUMBER}}$$

$$\text{MASS OF H}_2 = ?$$

$$\text{MOLE} = \frac{10^{20}}{6.022 \times 10^{23}}$$

$$\text{MASS OF O}_2 = ?$$

$$\text{MOLE} = 1.66 \times 10^{-4} \text{ MOLE}$$

$$\text{MASS OF CO}_2 = ?$$

$$\text{MASS OF H}_2 = \text{MOLES} \times \text{MOLAR MASS OF H}_2$$

$$\text{MASS OF H}_2 = 1.66 \times 10^{-4} \times 2$$

$$\boxed{\text{MASS OF H}_2 = 3.32 \times 10^{-4} \text{ g}} \quad \text{ANS.}$$

$$\text{MASS OF O}_2 = 1.66 \times 10^{-4} \times 32$$

$$\boxed{\text{MASS OF O}_2 = 5.33 \times 10^{-3} \text{ g}} \quad \text{ANS.}$$

$$\begin{aligned} \text{MASS OF CO}_2 &= \text{MOLES} \times \text{MWT OF CO}_2 \\ &= 1.66 \times 10^{-4} \times 44 \end{aligned}$$

$$\boxed{\text{MASS OF CO}_2 = 7.3 \times 10^{-3} \text{ g}} \quad \text{ANS.}$$

The masses of gases are not effected by pressure, and temperature. Thus their masses will remain unaffected by increasing pressure and temperature.

25 (a) Two moles of  $NF_3$  are enclosed in a 5 dm<sup>3</sup> flask at 27°C. Calculate the pressure exerted by the gas assuming that  
 i. gas behaves like an ideal gas  
 ii. gas behaves like a real gas  
 $a = 1.17 \text{ atm dm}^3 \text{ mol}^{-2}$   
 $b = 0.0371 \text{ dm}^3 \text{ mol}^{-1}$

(a) CONSIDERING IT AN IDEAL GAS.

$n = 2 \text{ MOLE}$      $V = 5 \text{ dm}^3$      $T = 27 + 273 = 300 \text{ K}$   
 $R = 0.0821$      $PV = nRT$   
 $P = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 300}{5}$

$P_{\text{IDEAL}} = 9.85 \text{ ATM}$  ANS.

(b) CONSIDERING IT A REAL GAS.

$a = 1.17 \text{ atm dm}^3 / \text{mol}^2$      $(P + \frac{a}{V^2} n^2)(V - nb) = nRT$   
 $b = 0.0371 \text{ dm}^3 / \text{mol}$      $(P + \frac{1.17 \times 2^2}{5^2})(5 - 2 \times 0.0371) = nRT$

$(P + 0.6872)(5 - 0.0742) = 2 \times 0.0821 \times 300$

$(P + 0.6872)(4.93) = 49.26$

$P + 0.6872 = \frac{49.26}{4.93}$

$P = 9.99 - 0.6872$

$P_{\text{REAL}} = 9.32 \text{ ATM}$  ANS

LESSONAD PRESSURE DUE TO FORCES OF ATTRACTION

is  $\Delta P = P_{\text{IDEAL}} - P_{\text{REAL}}$

$\Delta P = 9.85 - 9.32 = 0.52 \text{ ATM}$  ANS.

(c) IDEAL GAS

$P = \frac{nRT}{V}$   
 $P = \frac{2 \times 0.0821 \times 300}{40}$

$P = 1.2315 \text{ ATM}$

$\Delta P = 1.2315 - 1.22$

$\Delta P = 0.0115 \text{ ATM}$

REAL GAS

$(P + \frac{a}{V^2} n^2)(V - nb) = nRT$   
 $(P + \frac{1.17 \times 2^2}{40^2})(40 - 2 \times 0.0371) = 2 \times 0.0821 \times 300$

$(P + 0.0104)(39.92) = 49.26$

$P + 0.0104 = \frac{49.26}{39.92}$

$P + 0.0104 = 1.23$

$P = 1.23 - 0.0104$   
 $P = 1.22 \text{ ATM}$

In plain areas : 100°C  
 In Murree : 98°C  
 at Mount Everest : 69°C

} boiling points of water  
 at diff. altitudes.

The heat given to boiling liquids is latent heat of vaporization.

Significance of vacuum distillation

1. A liquid can be distilled without decomposition.
2. When boiling point is decreased less amount of energy is required.
3. Time required to distill a liquid is decreased.