Chapter 3

Gases

Boyle's Law

Statement

Boyle's law is stated as follows:-

The volume of a given mass of a gas at constant temperature is inversely proportional to the pressure applied to the gas.

Expression

$$V \propto 1/P \qquad (T \text{ \& } n \text{ constant})$$

$$V = k/P$$

$$PV = k \text{ ……. } (1)$$

'k' is proportionality constant.

The value of k is different for the different amounts of the same gas.

From eq (1) Boyle's law can be stated as:

The product of pressure and volume of a fixed amount of a gas at constant temperature is a constant quantity.

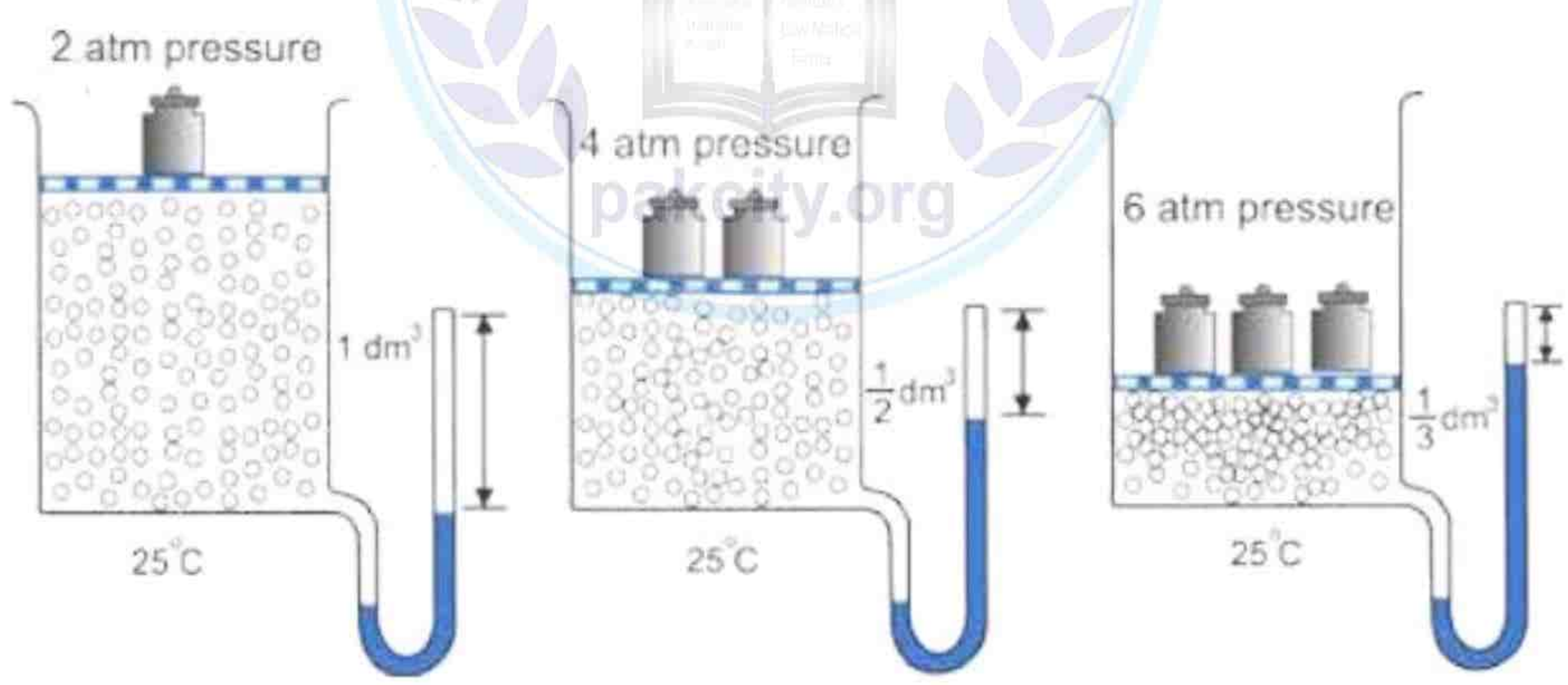
$$P_1V_1 = k \text{ and } P_2V_2 = k$$

$$P_1V_1 = P_2V_2$$

P_1= Initial value of pressure, V_1= Initial value of volume, P_2= Final value of pressure, V_2= Final value of volume

Experimental Verification of Boyle's Law

Let us take a gas in a cylinder having a moveable piston.



The cylinder is also attached with a manometer to read the pressure of the gas directly.

Experiment and Results

1. Let the initial volume of gas is 1 dm^3 and its pressure is 2 atmospheres when the piston has one weight on it.
2. When the piston is pressed twice with the help of two equal weights, the pressure becomes four atmospheres.
3. When the piston is loaded with a mass three times greater, then the pressure becomes six atmospheres.

Calculations

$$P_1V_1 = 2 \text{ atm} \times 1 \text{ dm}^3 = 2 \text{ dm}^3\text{atm} = k$$

$$P_2V_2 = 4 \text{ atm} \times 1/2 \text{ dm}^3 = 2 \text{ dm}^3\text{atm} = k$$

$$P_3V_3 = 6 \text{ atm} \times 1/3 \text{ dm}^3 = 2 \text{ dm}^3\text{atm} = k$$

Conclusion

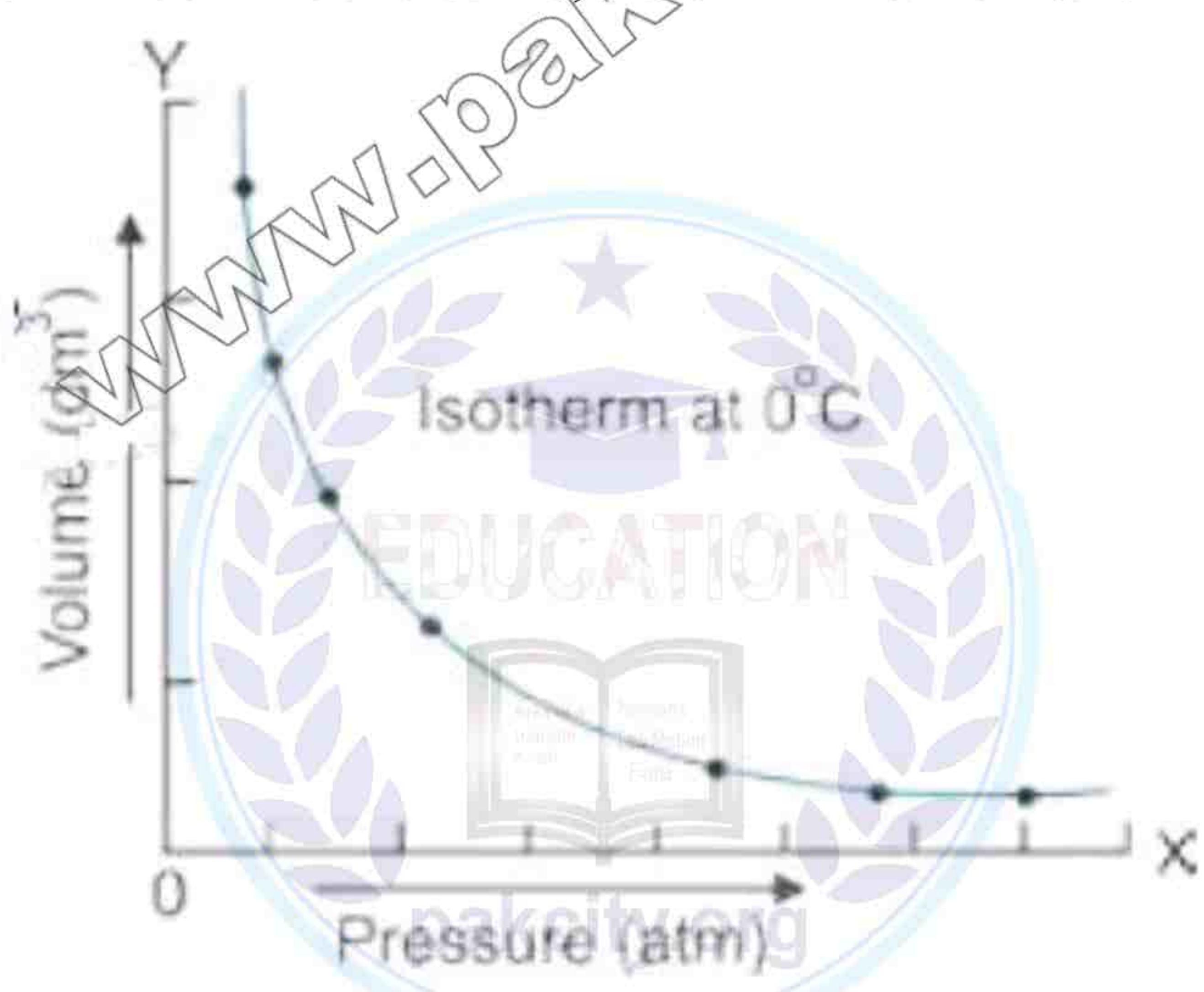
At constant temperature the volume of a given quantity of a gas is reduced in proportion to the increase in pressure.

Boyle's law is verified

Graphical Explanation of Boyle's Law

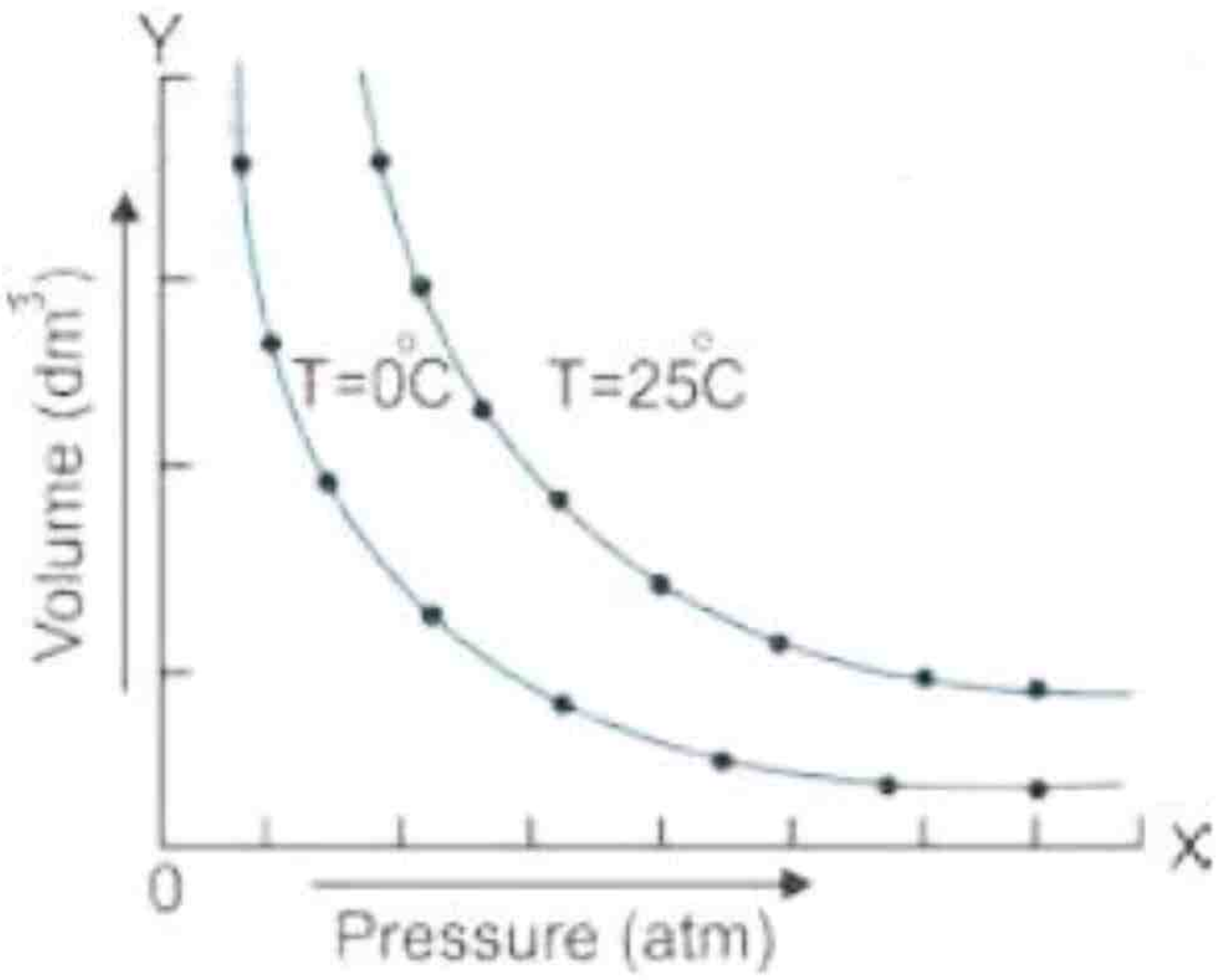
Plot of pressure and volume at 0 ºC

- Take a particular amount of a gas at a constant temperature say 0 ºC and enclose it in a cylinder having a piston in it.
- Increase in pressure decreases the volume.
- If a graph is plotted between pressure on the x-axis and volume on the y-axis, then a curve is obtained.
- This curve is called isotherm "iso" means same, "therm" means heat.



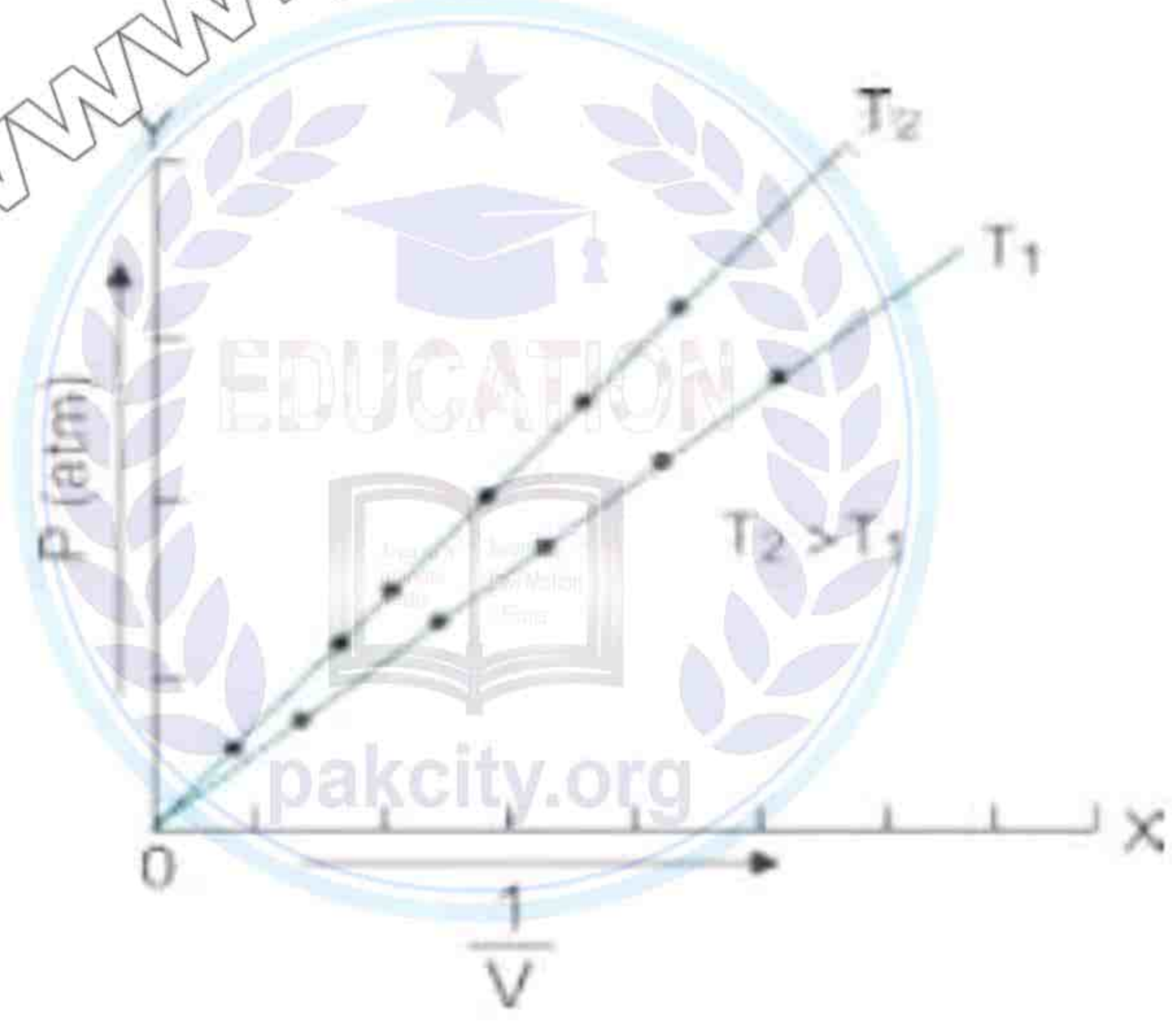
Plot of pressure and volume at 25 ºC

- Increase the temperature of the gas to 25°C.
- Keep this temperature constant and again vary the pressure and volume and plot the isotherm.
- It goes away from both the axes.
- The reason is that at higher temperature the volume of the gas has increased.



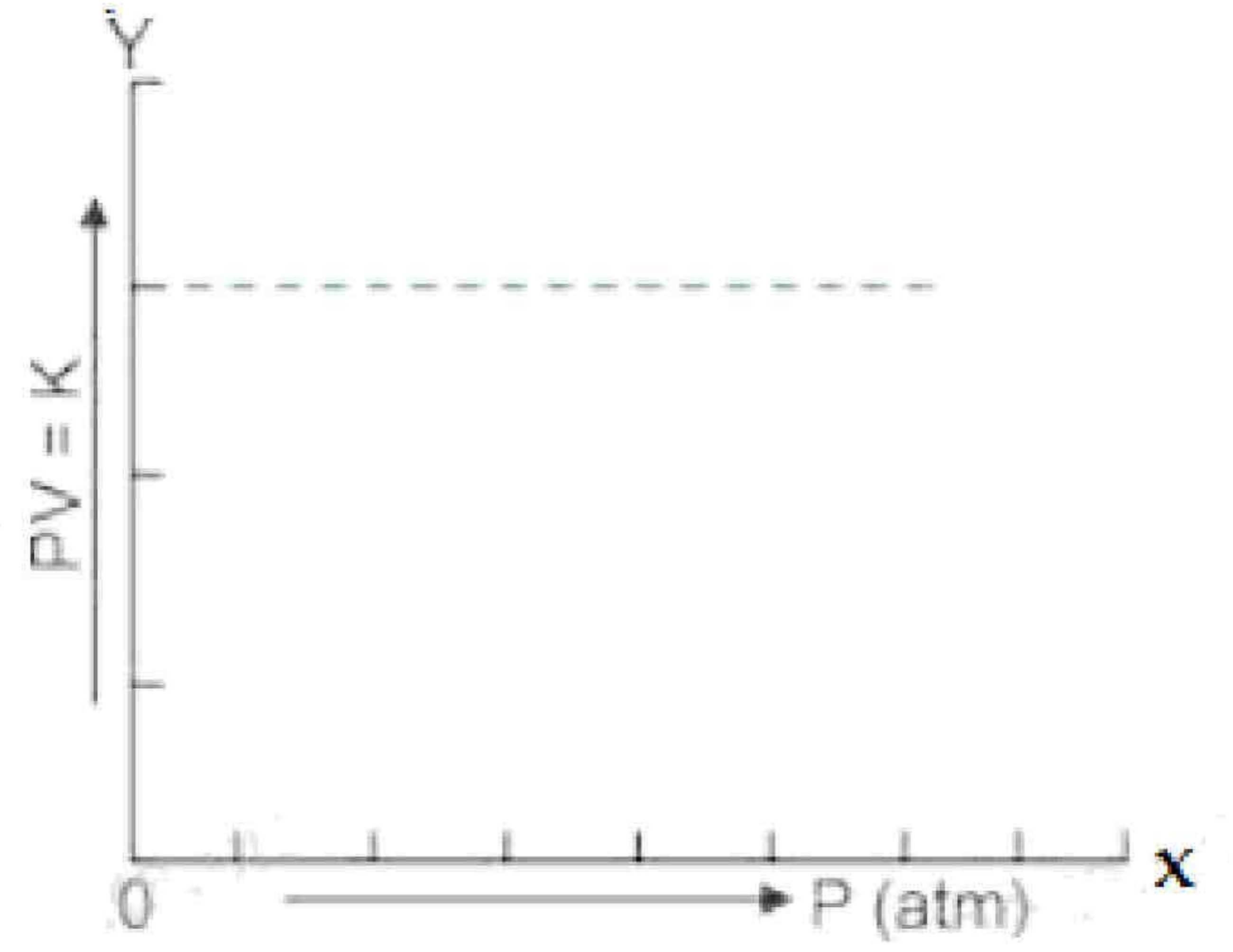
Plot of pressure and 1/volume

- If a graph is plotted between 1/V on x-axis and the pressure P on the y-axis then a straight line is obtained.
- This shows that the pressure and inverse of volume are directly proportional to each other.
- This straight line will meet at the origin which means that when the pressure is very close to zero, then the volume is so high that its inverse is very close to zero.
- By increasing the temperature of the same gas from T_1 to T_2 and keeping it constant, one can vary pressure and volume.
- The graph of this data between P and 1/V will give another straight line.
- This straight line at T_2 will be closer to the pressure-axis



Plot of PV and P

- Plot a graph between pressure on x-axis and the product PV on Y-axis.
- A straight line parallel to the pressure axis is obtained.
- This straight line indicates that 'k' is a constant quantity.
- At higher constant temperature, the volume increase and value of product PV should increase due to increase of volume at same pressure, but PV remains constant at this new temperature and a straight line parallel to the pressure axis is obtained.



Charles's Law

Statement

Charles's law is stated as:

The volume of the given mass of a gas is directly proportional to the absolute temperature when the pressure is kept constant.

Expression

$$V \alpha T \text{ (P \& n constant)}$$

$$V = kT$$

$$V/T = k$$

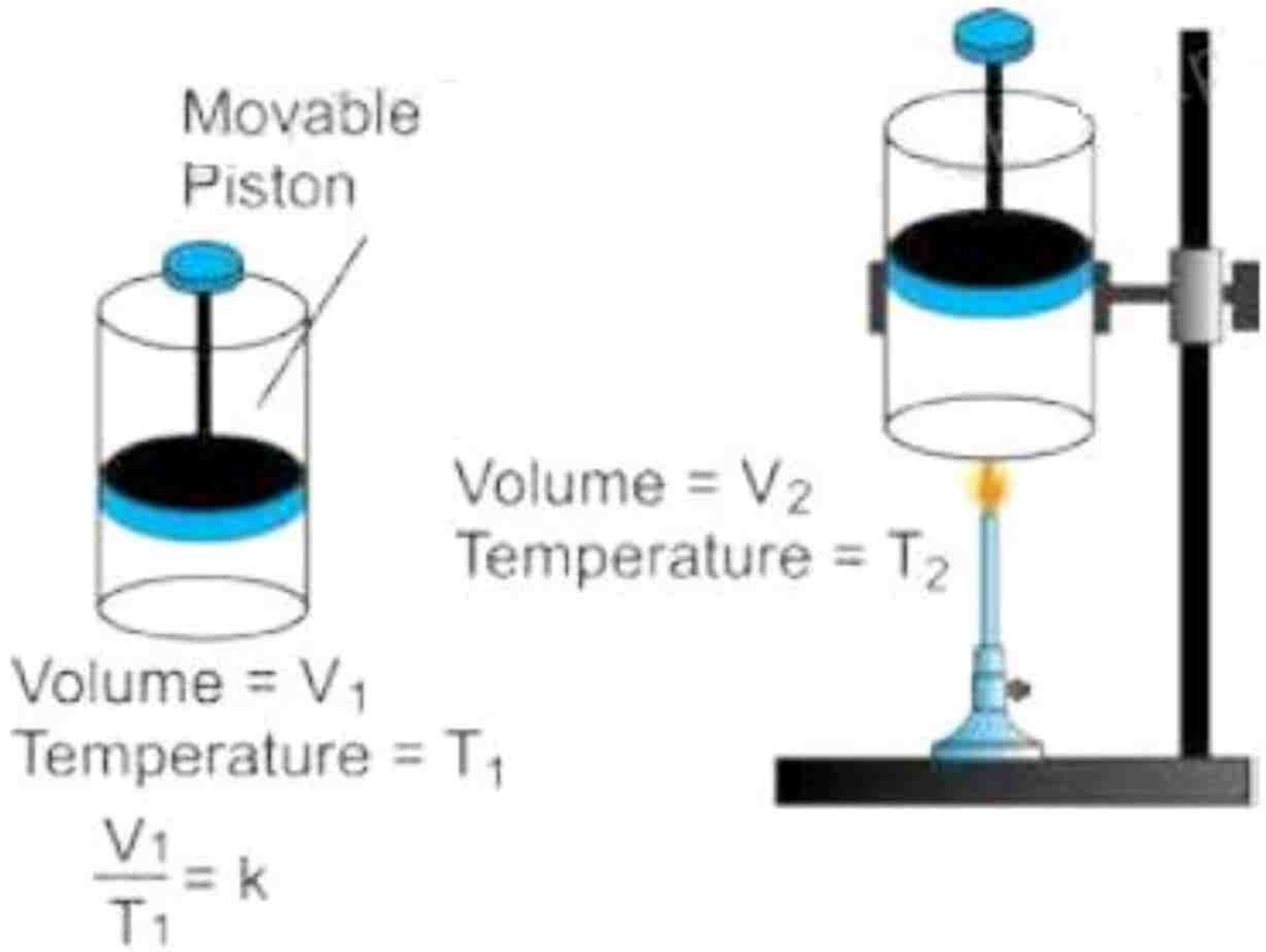
If the temperature is changed from T_1 to T_2 and volume changes from V_1 to V_2, then

$$V_1/T_1 = V_2/T_2 = k$$

$$V_1/T_1 = V_2/T_2$$

Experimental Verification of Charles's Law

Consider a certain amount of a gas enclosed in a cylinder fitted with a movable piston. The volume of the gas is V_1 and its temperature is T_1. When the gas in the cylinder is heated, both volume and the temperature of the gas increase.



The new values of volume and temperature are V_2 and T_2, respectively.

Conclusion

The ratio of volume to temperature remains constant for same amount of gas at same pressure.

Charles' law is verified

Derivation of Absolute Zero

Quantitative Definition of Charles's Law

At constant pressure, the volume of the given mass of a gas increases or decreases by 1/273 of its original volume at 0 ^oC for every 1 °C rise or fall in temperature, respectively.

General Equation for Calculating Volumes

$$V_t = V_o(1 + \frac{t}{273})$$

V_t= volume of gas at temperature T

V_o= volume of gas at 0 ^oC

t= Temperature on centigrade or Celsius scale

Celsius Scale does not Obey Charles' Law

Temperature volume data of a hypothetical gas is considered.

- At 0 ^oC the volume of the gas taken is 546 cm^3 which is twice of 273 cm^3.
- At 273 ^oC, the volume of the gas has doubled (1092 cm^3) and it should become practically zero at -273 ^oC.
- Since original volume is 546 cm^3, so, for 1 ^oC rise in temperature, 2 cm^3 increase in volume will take place.

- $2 cm^3$ is the 1/273 of 546 cm^3.
- For 100 ºC rise in temperature, a change of 200 cm^3 will take place.
- The volume does not increase corresponding to increase in temperature on Celsius scale.
- The increase in temperature from 10 ºC to 100 ºC increases the volume from 566 cm^3 to 746 cm^3.

$$V_1/T_1 = V_2/T_2$$

$$566/10 \neq 746/100$$

Charles's law is not obeyed if temperature is measured on Celsius scale

Kelvin Scale Obeys Charles's Law

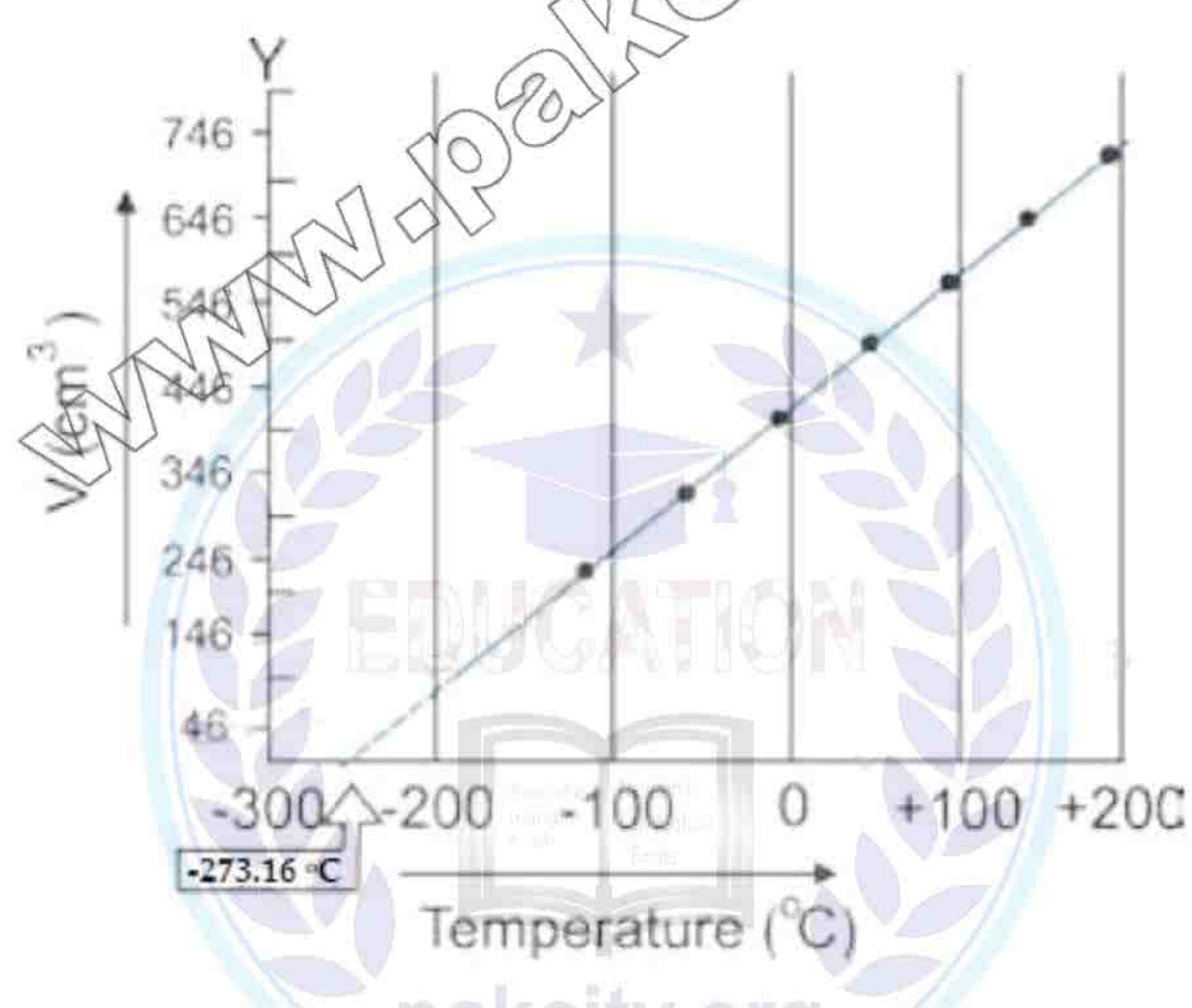
A new temperature scale was developed. It starts from 273 °C (more precisely -273.16 °C) which is called zero Kelvin or zero absolute.

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

$$\frac{566}{283} = \frac{746}{373} = 2 = K$$

- **Development of Kelvin Scale**

A graph is plotted between the variables of Charles's law.



If we plot a graph between temperature on x-axis and the volume of one mole of an ideal gas on y-axis, we get a straight line which cuts the temperature axis at -273.16 °C by extrapolation method.

Greater the mass of gas taken, greater will be the slope of straight line as there will be greater number of moles and volume.

Absolute Zero

The temperature of 0K or -273.16 ^oC is called absolute zero. This is the lowest possible temperature which would have been obtained if the substance remains in the gaseous phase. Actually all the gases are converted to liquid even before reaching this temperature. Real gases never attain this temperature.

General Gas Equation

Boyle's Law

According to Boyle's law:

$$V \propto \frac{1}{P} \text{ (when 'n' and 'T' are held constant)}$$

Charles's Law

According to Charles's law:

$$V \propto T \text{ (when n and P are held constant)}$$

Avogadro's Law

According to Avogadro's law:

$$V \propto n \text{ (when P \& T are held constant)}$$

Combining the three equations

$$V \propto \frac{nT}{P}$$

$$V = \text{Constant } \frac{nT}{P}$$

The constant is 'R' which is called **general gas constant**

$$V = R\frac{nT}{P}$$

$$PV = nRT$$

This is called an ideal gas equation or general gas equation.

Reduction to Individual Laws

$$PV = nRT\text{, when T and n are held constant, } PV = k \text{ (Boyle's law)}$$

$$V = R\,\frac{nT}{P}\text{, when P and n are held constant, } V = kT \text{ (Charles's law)}$$

$$V = R\,\frac{nT}{P}\text{ , when P and T are held constant } V = kn \text{ (Avogadro's law)}$$

For one mole of a gas

$$\mathbf{PV = RT \text{ or } PV/T = R}$$

The ratio of PV to T is a constant quantity (molar gas constant)

$$\mathbf{P_1V_1/T_1 = R \quad P_2V_2/T_2 = R}$$

Therefore,

$$P_1V_1/T_1 = P_2V_2/T_2$$

Calculation of Ideal Gas Constant

According to STP

The volume of one mole of an ideal gas at STP (one atmospheric pressure and 273.16 K) is 22.414 dm^3.

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

$$R = \frac{1 \text{ atm} \times 22.414 \text{ dm}^3}{1 \text{ mole} \times 273.16 \text{ K}}$$

$$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

Physical meaning of R

If we have one mole of an ideal gas at 273.16 K and one atmospheric pressure and its temperature is increased by 1 K, then it will absorb 0.0821 dm^3 -atm of energy, dm^3 -atm is the unit of energy in this situation.

Pressure in mm of mercury or torr and the volume in cm^3

$R = 0.0821 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$

$= 0.0821 \times 760 \text{ dm}^3 \text{ mm Hg K}^{-1} \text{ mol}^{-1}$

$= 62.4 \text{ dm}^3 \text{ mm Hg K}^{-1} \text{ mol}^{-1}$ Since, (1 mm o f Hg = 1 to rr)

$= 62.4 \text{ dm}^3 \text{ torr K}^{-1} \text{ mol}^{-1}$

$= 62400 \text{ cm}^3 \text{ torr K}^{-1} \text{ mol}^{-1}$ As, ($1 \text{ dm}^3 = 1000 \text{ cm}^3$)

According to SI units

The SI units of pressure are Nm^{-2} and of volume are m^3. By using Avogadro's principle:

1 atm = 760 torr = 101 325 Nm^{-2}

lm^3 = 1000 dm^3

n = 1 mole

T = 273.16 K

P = 1 atm = 101325 Nm^{-2}

V = 22.414 dm^3 = 0.022414 m^3

Putting their values, alongwith units.

$$R = \frac{PV}{nT} = \frac{101325\ N\ m^{-2}\ x\ 0.0224l\ m^3}{1\ mol\ x\ 273.16\ K}$$

$$R = 8.3143\ Nm\ K^{-1}\ mol^{-1} = 8.3143\ J\ K^{-1}\ mol^{-1}\ (1\ Nm = 1J)$$

Since 1cal. = 4.18 J

$$\text{so } R = \frac{8.3143}{4.18} = 1.989 cal\ K^{-1}\ mol^{-1}$$

Dalton's Law of Partial Pressures

Statement

The total pressure exerted by a mixture of non-reacting gases is equal to the sum of their individual partial pressures.

Explanation

Let the gases are designated as 1,2,3, and their partial pressures are p_1, p_2, p_3. The total pressure (P_t) of the mixture of gases is given by:

$$P_t = p_1 + p_2 + p_3$$

Partial pressure

The partial pressure of a gas in a mixture of gases is the pressure that it would exert on the walls of the container, if it were present all alone in that same volume under the same temperature.

Example

Take four cylinders of 10 dm^3 each and three gases H_2, CH_4 and O_2 are separately enclosed in first three of them at the same temperature. Let their partial pressures be 400 torr, 500 torr and 100 torr, respectively. All these gases are transferred to a fourth cylinder of capacity 10 dm^3 at the same temperature. According to Dalton's law:

$$P_t = p_{H2} + p_{CH4} + p_{O2} = (400 + 500 + 100)\ torr$$

$$P_t = 1000\ torr$$

The total pressure is the result of total number of collisions per unit area in a given time.

Application of general gas equation to individual gases

Adding these three equations

$$P_t = p_{H_2} + p_{CH_4} + p_{O_2}$$

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

$$P_t = n_t \frac{RT}{V} \qquad \text{where } n_t = n_{H_2} + n_{CH_4} + n_{O_2}$$

$$P_tV = n_tRT$$

The total pressure of the mixture of gases depends upon the total number of moles of the gases.

Calculation of Partial Pressure of a Gas

Suppose we have a mixture of gas A and gas B. This mixture is enclosed in a container having volume (V). The total pressure is one atm. The number of moles of the gases A and B are n_A and n_B, respectively. If they are maintained at temperature T, then

$P_tV= n_tRT$….. (equation for the mixture of gases)

$p_AV= n_ART$…….(equation for gas A)

$p_BV= n_BRT$……..(equation for gas B)

Divide the first two equations

$$\frac{p_AV}{P_tV} = \frac{n_ART}{n_tRT}$$

$$\frac{p_A}{P_t} = \frac{n_A}{n_t}$$

$$p_A = \frac{n_A}{n_t} P_t$$

$$p_A = x_A \; P_t \qquad (x_A \text{ is mole fraction of gas A})$$

$$p_B = x_B \; P_t$$

Partial pressure of a gas is the mole fraction of that gas multiplied by the total pressure of the mixture. Mole fraction of any one gas in the mixture is less than unity. The sum of mole fractions is always equal to unity.

Applications of Dalton's Law of Partial Pressures

1. Collection of gases over water

Some gases are collected over water in the laboratory. The gas during collection gathers water vapours and becomes moist. The pressure exerted by this moist gas is the sum of the partial pressures of the dry gas and water vapours. The partial pressure exerted by the water vapours is called aqueous tension.

$$P_{moist} = p_{dry} + p_{w.vap}$$

$$P_{moist} = p_{dry} + \text{aqueous tension}$$

$$p_{dry} = P_{moist} - \text{aqueous tension}$$

2. Process of respiration

The process of respiration depends upon the difference in partial pressures. When animals inhale air then oxygen moves into lungs as the partial pressure of oxygen in the air is 159 torr, while the partial pressure of oxygen in the lungs is 116 torr. Carbon dioxide produced during respiration moves out in the opposite direction, as its partial pressure is more in the lungs than that in air.

3. Breathing at higher altitudes

At higher altitudes, the pilots feel uncomfortable breathing because the partial pressure of oxygen in the un-pressurized cabin is low, as compared to 159 torr, where one feels comfortable breathing.

4. Breathing under sea

Deep sea divers take oxygen mixed with an inert gas say He and adjust the partial pressure of oxygen according to the requirement. In sea, after every 100 feet depth, the diver experiences approximately 3 atm pressure, so normal air cannot be breathed in depth of sea. The pressure of N_2 increases in depth of sea and it diffuses in the blood.

Graham's Law of Diffusion

Statement

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

Expression

$$\text{Rate of diffusion} \propto \frac{1}{\sqrt{d}} \quad \text{(at constant temperature and pressure)}$$

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

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

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

The constant k is same for all gases, when they are all studied at the same temperature and pressure.

Explanation

Let us have two gases 1 and 2, having rates of diffusion as r_1 and r_2 and densities as d_1 and d_2 respectively.

According to Graham's law

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

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

Divide the two equations and rearrange

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

The density of a given gas is directly proportional to its molecular mass. Graham's law of diffusion can also be written as follows:

$$\frac{r_1}{r_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Where M_1 and M_2 are the molar masses of gases.

Demonstration of Graham's Law

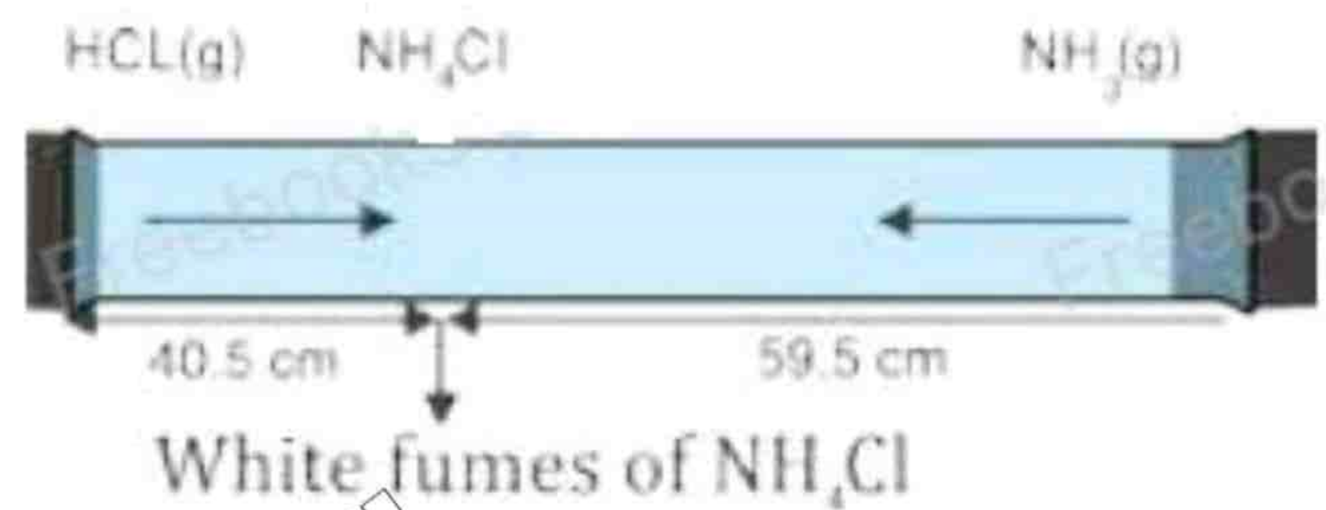
1. Two cotton plugs soaked in HCl and NH_3 solutions are introduced in the open ends of 100 cm long tube simultaneously.
2. HCl molecules travel a distance of 40.5 cm while NH_3 molecules cover 59.5 cm in the same duration.
3. They produce dense white fumes of ammonium chloride at the point of junction.

Calculations through Law

$$\frac{r_{NH_3}}{r_{HCl}} = \frac{\sqrt{M_{HCl}}}{\sqrt{M_{NH_3}}}$$

$$\frac{59.5}{40.5} = \frac{\sqrt{36.5}}{\sqrt{17}}$$

$$1.46 = 1.46$$



Graham's Law is verified

Kinetic Molecular Theory of Gases

History

For illustrating the behaviour of gases quantitatively, Bernoulli (1738) put forward kinetic molecular theory of gases. Clausius (1857) derived the kinetic equation and deduced all the gas laws from it. The theory was elaborated and extended by Maxwell, who gave the law of distribution of velocities. Boltzmann also contributed and studied the distribution of energies among the gas molecules. Among some other names Van der Waal is the prominent scientist in this field.

Postulates of Kinetic Molecular Theory

1. Every gas consists of a large number of very small particles called molecules. Gases like He, Ne, Ar have monoatomic molecules.
2. The molecules of a gas move haphazardly, colliding among themselves and with the walls of the container and change their directions.
3. The pressure exerted by a gas is due to the collisions of its molecules with the walls of a container. The collisions among the molecules are perfectly elastic.
4. The molecules of a gas are widely separated from one another and there are sufficient empty spaces among them.
5. The molecules of a gas have no forces of attraction for each other.
6. The actual volume of molecules of a gas is negligible as compared to the volume of the gas.
7. The motion imparted to the molecules by gravity is negligible as compared to the effect of the continued collisions between them.
8. The average kinetic energy of the gas molecules varies directly as the absolute temperature of the gas.

Kinetic Equation of Gas

R.J Clausius deduced an expression for the pressure of an ideal gas. Due to the collisions of gas molecules, a force is exerted on the walls of the container. This force when divided by the area of the vessel gives force per unit area, which is called pressure. In this way, the final form of kinetic equation is as follows:

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

P = pressure
V = volume
m = mass of one molecule of the gas
N = number of molecules of gas in the vessel
$\overline{c^2}$ = mean square velocity

Explanation of Gas Laws from Kinetic Theory of Gases

(a) Boyle's Law

The kinetic energy is directly proportional to the absolute temperature of the gas. The kinetic energy of N molecules is:

$$\frac{1}{2} mN\overline{c^2}$$

$$\frac{1}{2} mN\overline{c^2} \propto T$$

$$\frac{1}{2} mN\overline{c^2} = kT$$

Where k is the proportionality constant. According to the kinetic equation of gases:

$$PV = \frac{1}{3} mN\overline{c^2}$$

Multiplying and dividing by 2 on right hand side

$$PV = \frac{2}{3}\left(\frac{1}{2} mN\overline{c^2}\right)$$

$$PV = \frac{2}{3} kT$$

If the temperature (T) is constant then right hand side of equation 2/3 kT is constant. Let that constant be k'.

So, PV = k' (which is Boyle's law)

Hence at constant temperature and number of moles, the product PV is a constant quantity.

(b) Charles' Law
Consider the following equation:

$$PV = \frac{2}{3}\ kT$$

$$V = \frac{2}{3}\ \frac{kT}{P} = (\frac{2k}{3P})\ T$$

At constant pressure. Therefore,

$$\frac{2k}{3P} = k" \text{ (a new constant)}$$

$$V = k"\,T$$

$$\frac{V}{T} = k" \text{ (which is Charles's law)}$$

(c) Avogadro's Law

Consider two gases 1 and 2 at the same pressure P and having the same volume V. Their number of molecules are N_1 and N_2, masses of molecules are m_1 and m_2 and mean square velocities are $\overline{c_1^2}$ $\overline{c_2^2}$
Their kinetic equations can be written as follows:

$$PV = \frac{1}{3}\ m_1 N_1 \overline{c_1^2} \quad \text{for gas(1)}$$

$$PV = \frac{1}{3}\ m_2 N_2 \overline{c_2^2} \quad \text{for gas(2)}$$

$$\text{Equalizing}\ \ \frac{1}{3}\ m_1 N_1 \overline{c_1^2} = \frac{1}{3}\ m_2 N_2 \overline{c_2^2}$$

$$\text{Hence,}\ \ m_1 N_1 \overline{c_1^2} = m_2 N_2 \overline{c_2^2} \quad \ldots \text{(eq 1)}$$

When the temperature of both gases is the same, their mean kinetic energies per molecule will also be same, so

$$\frac{1}{2}\ m_1 \overline{c_1^2} = \frac{1}{2}\ m_2 \overline{c_2^2}$$

$$m_1 \overline{c_1^2} = m_2 \overline{c_2^2} \quad \text{(eq 2)}$$

Dividing eq (1) by eq (2)

$$N_1 = N_2$$

Equal volumes of all the gases at the same temperature and pressure contain equal number of molecules, which is Avogadro's law.

(d) Graham's Law of Diffusion

$$PV = \frac{1}{3} mN\overline{c^2}$$

Applying the kinetic equation

$$PV = \frac{1}{3} mN_A\overline{c^2}$$

If we take one mole of a gas having Avogadro's number of molecules (N = NA) then the equation can be written as:

$$PV = \frac{1}{3} M\overline{c^2} \quad (M = mN_A)$$

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

Where M is the molecular mass of the gas. Taking square root:

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

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{d}} \quad (\frac{M}{V} = d)$$

'V' is the molar volume of gas at given conditions. Since the root mean square velocity of the gas is proportional to the rate of diffusion of the gas.

$$\sqrt{\overline{c^2}} \propto r$$

$$r \propto \sqrt{\frac{3P}{d}}$$

At constant pressure

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

Graham's law verified.

Kinetic Interpretation of Temperature

According to kinetic molecular theory of gases the molecules of a gas move randomly with elastic collisions. The kinetic equation of gases can be re-written as:

$$PV = \frac{1}{3} mN\overline{c^2}$$

Here m is the mass of one molecule of the gas, N is the number of molecules in the vessel and $\overline{c^2}$ is their mean square velocity. The average kinetic energy associated with one molecule of a gas due to its translational motion is given by the following equation.

$$E_k = \frac{1}{2} m\overline{c^2}$$

(eq 1)

E_k is the average translational kinetic energy of gas molecules.

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

(eq 2)

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

To get insight into the meaning of temperature consider one mole of a gas.

$$N = N_A$$

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

According to the general gas equation for one mole of a gas

$$PV = RT$$

Hence,

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

$$E_k = \frac{3R}{2N_A} T$$

A new definition of temperature

The kelvin temperature of a gas is directly proportional to the average translational kinetic energy of its molecules. This suggests that a change in temperature means change in the intensity of molecular motion.

Linde's Method of Liquefaction of Gases

Principle

Joule-Thomson Effect

When a compressed gas is allowed to expand into a region of low pressure it gets cooled.

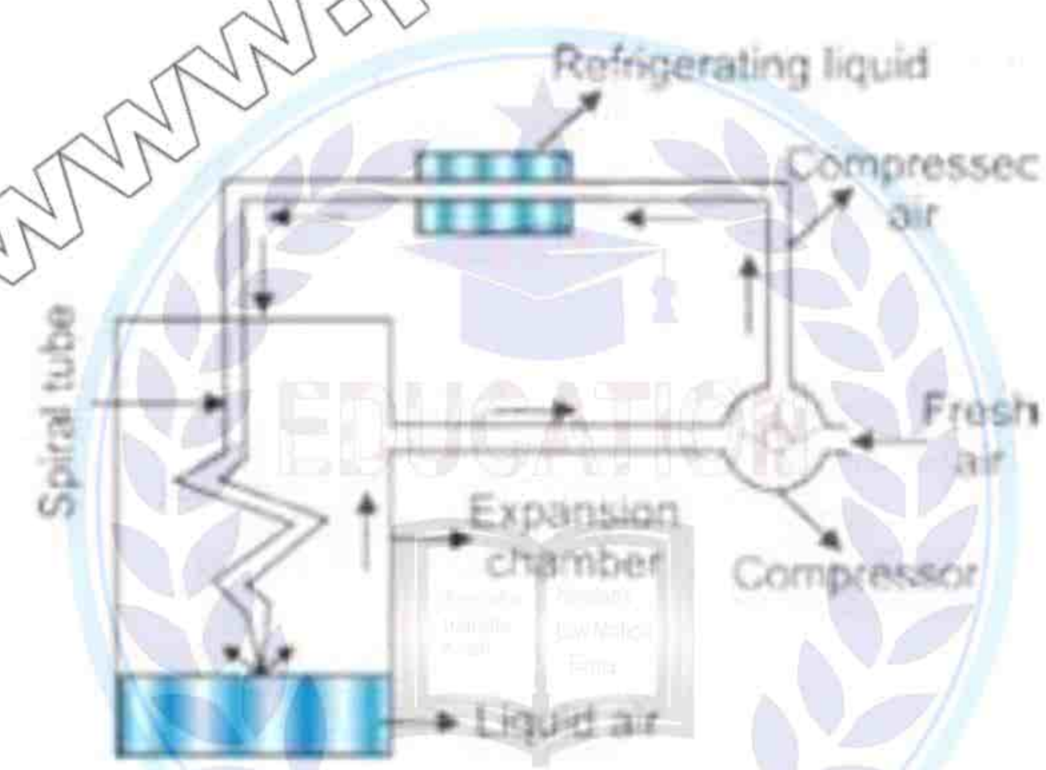
Assembly

The assembly consists of the following parts:

1. Compressor
2. Refrigerating liquid
3. Spiral tube
4. Expansion chamber

Working

1. Air is compressed to about 200 atmospheres.
2. It is passed though water cooled pipe where the heat of compression is removed.
3. It is then allowed to pass through a spiral pipe having a jet at the end.
4. When the air comes out of the jet the expansion takes place from 200 atm to 1 atm leading to fall of temperature.



5. This cooled air goes up and cools the incoming compressed air.
6. It returns to the compression pump.
7. This process is repeated again and again.
8. The liquid air is collected at the bottom of the expansion chamber.

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

Van der Waals Equation for Real Gases

Volume Correction

Compression of gas

When a gas is compressed, the molecules are pushed so close together that the repulsive forces operate between them.

The molecules have definite volume, no doubt very small as compared to the vessel, but it is not negligible.

Van der Waals postulated that the actual volume of molecules can no longer be neglected in a highly compressed gas.

b= The effective volume of the molecules per mole of a gas

b= excluded volume which is constant and characteristic of a gas. Its value depends upon the size of gas molecules.

The volume available to gas molecules is the volume of the vessel minus the volume of gas molecules.

$$V_{free} = V_{vessel} - b$$

V_{free}= volume available to the gas molecules.

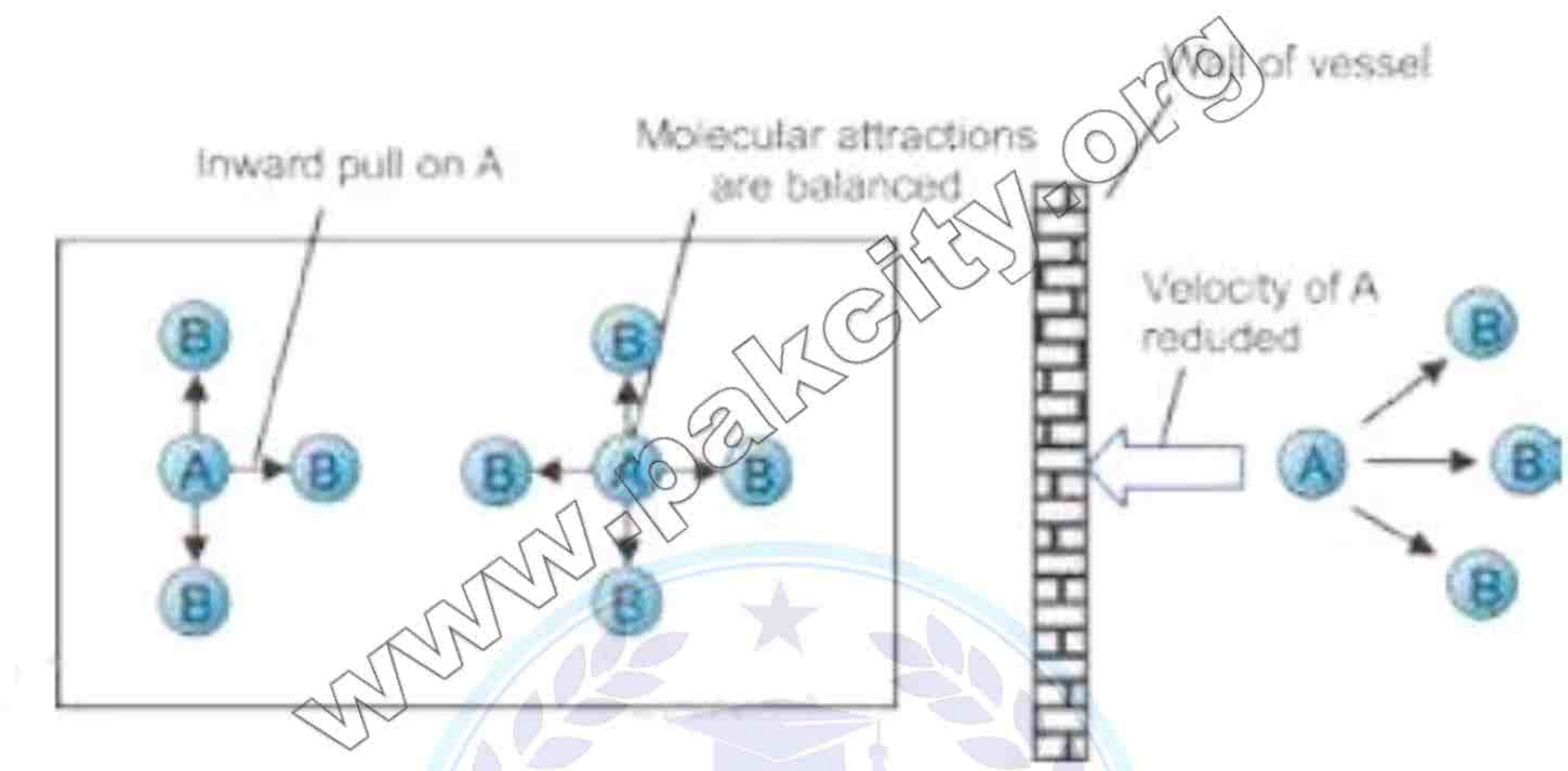
The excluded volume b is not equal to the actual volume of gas molecules.

It is four times the actual volume of molecules.

$$b = 4V_m$$

V_m= volume of one mole of gas molecules in a highly compressed state but not liquid state.

Pressure Correction



A molecule in the interior of a gas is attracted by other molecules on all sides, so the attractive forces are cancelled out. When a molecule strikes the wall of a container, it experiences a force of attraction towards the other molecules in the gas. This decreases the force of its impact on the wall.

Explanation

Consider the molecule "A" which is unable to create pressure on the wall due to the presence of attractive forces due to 'B' type molecules. Let the observed pressure on the wall of the container is P. This pressure is less than the actual pressure Pi, by an amount P', so

$$P = P_i - P'$$

P_i= true kinetic pressure if the forces of attraction would have been absent.

P’= lessened pressure due to attractive forces

$$P_i = P + P'$$

The pressure P for one mole of a gas used up against intermolecular attractions should decrease as volume increases. The value of P' in terms of a constant 'a' which accounts for the attractive forces and the volume V of vessel can be written as:

$$P' = \frac{a}{V^2}$$

Proof
P’ is determined by the forces of attraction between molecules of type A, which are striking the wall of the container and molecules of type B, which are pulling them inward. The net force of attraction is proportional to the concentrations of A type and B type molecules.

$$P' \infty C_A . C_B$$

n= the number of moles o f A and B separately and total volume of both types of molecules is ‘V’.
V= total volume of both types of molecules
n/V= moles dm^{-3}

$$P' \quad \infty \quad \frac{n}{V} . \frac{n}{V}$$

$$P' \quad \infty \quad \frac{n^2}{V^2}$$

$$P' \quad \infty \quad \frac{an^2}{V^2}$$

‘a’ is a constant of proportionality

If, n = 1 (one mole of gas)

$$P' = \frac{a}{V^2}$$

Greater the attractive forces among the gas molecules, smaller the volume of vessel, greater the value of lessened pressure P’.
a= coefficient of attraction or attraction per unit volume. It has a constant value for a particular real gas.

$$P_i = P + \frac{a}{V^2}$$

Van der Waal’s Equation
Putting the values in PV = nRT

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

For 'n' moles of a gas $$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

Units of a

$$P' = \frac{n^2a}{V^2}$$

$$a = \frac{P'V^2}{n^2}$$

$$a = \frac{atm \times (dm^3)^2}{(mol)^2}$$

$$a = atm\ dm^6\ mol^{-2}$$

In S.I. units, pressure is in Nm^{-2} and volume in m^3

$$a = \frac{Nm^{-2} \times (m^3)^2}{(mol)^2}$$

$$a = Nm^{+4}\ mol^{-2}$$

Units of b

$dm^3\ mol^{-1}$ or $m^3\ mol^{-1}$

Plasma State

Plasma is the "fourth state of matter". Plasma was identified by the English scientist William Crookes in 1879.

Definition

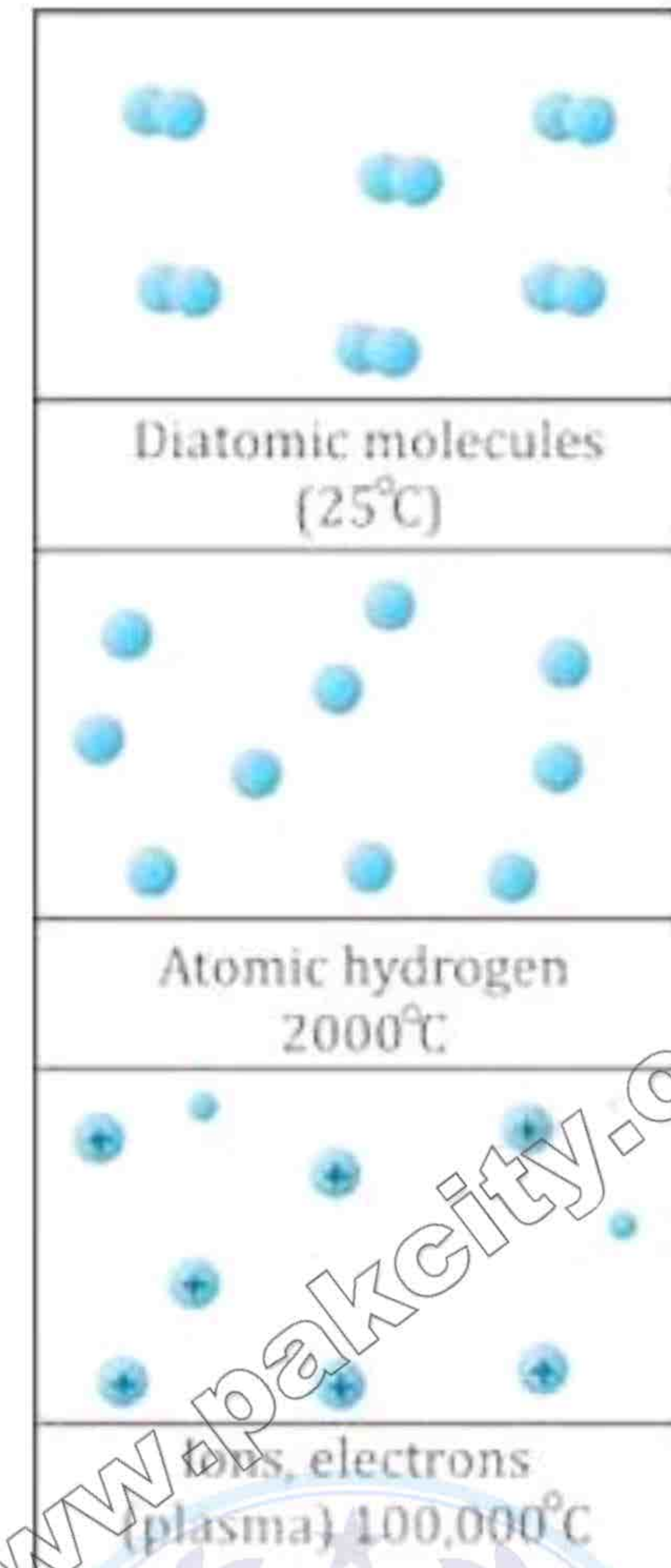
The ionized gas mixture, consisting of ions, electrons and neutral atoms is called plasma.

OR

Plasma is a distinct state of matter containing a significant number of electrically charged particles a number sufficient to affect its electrical properties and behaviour.

Formation of Plasma

When more heat is supplied, the atoms or molecules may be ionized. The atom loses one electron and develops a net positive charge. It becomes an ion. In a sufficiently heated gas, ionization happens many times, creating clouds of free electrons and ions. All the atoms are not ionized, and some of them remain completely intact with no net charge.



Natural and Artificial Plasma

Characteristics of Artificial Plasma

Artificial plasma can be created by ionization of a gas as in neon signs.

Plasma at low temperatures is hard to maintain because outside a vacuum low temperature plasma reacts rapidly with any molecule it encounters.

Characteristics of Natural Plasma

Natural plasma exists only at very high temperatures, or low temperature vacuums.

Natural plasma does not breakdown or react rapidly, but is extremely hot (over 20,000°C minimum).

Their energy is so high that they vaporize any material they touch.

Characteristics of Plasma

1. Electromagnetically responsive

Plasma must have sufficient number of charged particles. It exhibits a collective response to electric and magnetic fields. The motion of the particles in the plasma generates fields and electric currents from within plasma density. It refers to the density of the charged particles. This complex set of interactions makes plasma a unique, fascinating, and complex state of matter.

2. Macroscopically neutral

It is macroscopically neutral. In measurable quantities the number of electrons and ions are equal.

Existence of Plasma

1. Entire universe is almost of plasma.
2. Plasmas are found in everything from the sun to quarks.
3. It is the stuff of stars. A majority of the matter in inner-stellar space is plasma.

4. The sun is a 1.5 million kilometer ball of plasma heated by nuclear fusion.
5. On earth it only occurs in a few limited places, like lightning bolts, flames, auroras, and fluorescent lights.
6. When an electric current is passed through neon gas, it produces both plasma and light.

Applications of Plasma

In fluorescent light bulbs

Inside the long tube of a fluorescent light bulb is a gas. When the light is turned on, electricity flows through the tube. This electricity charges up the gas. This charging and exciting of the atoms creates a glowing plasma inside the bulb.

In neon signs

Neon signs are glass tubes filled with gas. When they are turned on then the electricity flows through the tube. The electricity charges the gas and creates a plasma inside the tube. The plasma glows with a special colour depending on what kind of gas is inside.

Generation of electrical energy

It generates electrical energy from fusion pollution control and removal of hazardous chemicals.

Use in offices and homes

Plasma light up our offices and homes, make our computers and electronic equipment work.

Use in lasers and particle accelerator

They drive lasers and particle accelerators, help to clean up the environment, pasteurize foods and make tools corrosion-resistant.

Miscellaneous uses

They find applications such as plasma processing of semiconductors, sterilization of some medical products, lamps, lasers, diamond coated films, high power microwave sources and pulsed power switches.

Future Horizons

The application of magnetic fields involves the use of plasma. The magnetic fields create low energy plasma which create molecules in metastable state. These metastable molecules survive long enough to react with designated molecules and are selective in their reactivity. They give solution to radioactive contamination. Scientists are experimenting with mixtures of gases to work as metastable agents on plutonium and uranium.

Numericals

5. (b) A sample of carbon monoxide gas occupies 150.0ml at 25.0^{0}C. It is then cooled at constant pressure until it occupies 100.0 ml. What is the new temperature?

Data:

$V_1 = 150\ cm^3$

$T_1 = 25^oC + 273 = 298K$

$V_2 = 100\ cm^3$

To Find: $T_2 = ?$

Formula:

Using the equation from Charles's law

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

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

$$T_2 = \frac{100 \times 298}{150} = \mathbf{198.6\ K}$$

As $K = {}^oC + 273$

${}^oC = K - 273 = 198.6 - 273 = \mathbf{-74.3^0C}$

16. Helium gas in 100cm^3 container at a pressure of 500 torris transferred to a container with a volume of 250 cm^3. What will be the new pressure?

(a) No change in temperature occurs (Isothermal: Boyle's Law)

Data:
Initial volume of He gas $=V_1=100cm^3$
Initial pressure of He gas $=P_1=500$ torr
Final volume of He gas $=V_2=250\ cm^3$
To Find: Final pressure of He gas $= P_2= ?$

Formula: $P_1V_1= P_2V_2$

Solution: $P_2= \frac{P_1V_1}{V_2}$

$$P_2 = \frac{500\ torr \times 100\ cm^3}{250cm^3}$$

P_2**=200 tor**

(b) When the temperature changes from $T_1 = 20^oC$ to $T_2 = 15^oC$. Then general gas equation for one mole is to be applied.

$T_1 = 20^oC$
$T_2 = 15^oC$
$T_1 = 20^oC + 273 = 293\ K$
$T_2 = 15^oC + 273 = 288\ K$

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

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2}$$

$$P_2 = \frac{500\times100}{293} \times \frac{288}{250}$$

$=$ **196.58 torr**

17. What are the densities in Kgm^{-3} for following gases at S.T.P (P = 101325 Nm^{-2} T = 273 K, Molecular mass are in $Kg.mol^{-}$(i)Methane (ii)Oxygen(iii)Hydrogen

(i)

Data: Temperature of CH_4 = 273 K
Pressure of CH_4 = 101325 Nm^{-2}
General gas constant R = 8.3143 $JK^{-}mol^{-}$

Convert gram into kilogram
Molar mass of CH_4 = 16 $gmol^{-}$
= 16×10^{-3} kg mol

Formula: $d = \frac{PM}{RT}$

Soultion:

$$d = \frac{101325Nm^{-2}\times16 \times10^{-3}\ kg\ mol^{-1}}{8.3143JK^{-1}\ mol^{-1}\times273K}$$

$$d = \frac{101325Nm^{-2} \times 16 \times 10^{-3}\ kg}{8.3143 \times 273Nm}$$

As J = N.m

$$d = \frac{1621.2}{2269.8}$$

$= \mathbf{0.714\ kg\ m^{-3}}$

(ii)

Data: Convert gram into kilogram

Molar mass of O_2 = 32 $gmol^{-1}$

= 32×10^{-3} kg mol^{-1}

Formula: $d = \frac{PM}{RT}$

Solution:

$$d = \frac{101325Nm^{-2} \times 2 \times 10^{-3}\ kg\ mol^{-1}}{8.3143JK^{-1}\ mol^{-1} \times 273K}$$

$$d = \frac{101325 \times 2 \times 10^{-3}}{8.3143 \times 273K}\ \frac{Nm^{-2} \times kg}{J}$$

Since J = Nm

$$d = \frac{3242.4}{2269.8}\ Kgm^{-3}$$

$= \mathbf{1.428\ kg\ m^{-3}}$

(iii)

Data: Convert gram into kilogram

Molar mass of H_2= 2 $gmol^{-1}$

= 2×10^{-3} kg mol^{-1}

Formula: $d = \frac{PM}{RT}$

Solution: $d = \frac{101325Nm^{-2} \times 2 \times 10^{-3}\ kg\ mol^{-1}}{8.3143JK^{-1}\ mol^{-1} \times 273K}$

$$d = \frac{101325 \times 2 \times 10^{-3}}{8.3143 \times 273K}\ \frac{Nm^{-2} \times kg}{J}$$

Since J = Nm

$$d = \frac{202.65}{2269.8}$$

$= \mathbf{0.089\ kgm^{-3}}$

Compare the values of densities in proportion to their mole masses.

Ans.

$\mathbf{d_{H_2}}$	:	$\mathbf{d_{CH_4}}$	:	$\mathbf{d_{O_2}}$
0.089	:	0.714	:	1.428
0.089/0.089	:	0.714/0.089	:	1.428/0.089
1	:	8	:	16

How do you justify that increase of volume up to 100 dm^3 at 27°C of 2 moles of NH_3 will allow the gas behave ideally, as compared to S.T.P conditions.

Ans.

2 moles of NH_3 at 0°C and 1 atm pressure will be having volume around 44.828 dm^3. Under these conditions it will be close to ideal behavior, but not perfect ideal. The reason is that NH_3 is a polar gas and same forces of attractions are present at 0°C.

When the temperature is increased to 27°C and volume is increased upto 100 dm^3 , then NH_3 will definitely behave more ideally.

18. A sample of Krypton with a volume of 6.25 dm^3 and a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm^3 and a pressure of 375 torr. What will be its final temperature (in °C)

Data:

Initial volume of gas = V_1= 6.25 dm^3
Initial pressure of gas = P_1 =765 torr
Initial pressure of gas = T_1=20°C
Final volume of gas = V_2= 9.55 dm^3
Final pressure of gas=P_2 =375 torr

Initial pressure of gas = T_1 =20°C + 273
= 293 K

To Find: Final temperature of gas = T_2= ?

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

Solution: $$T_2 = \frac{P_2V_2}{P_1V_1} \times T_1$$

$$T_2 = \frac{375\text{torr} \times 9.55\ dm^3 \times 293K}{765\ \text{torr} \times 6.25dm^3}$$

$$= \frac{375 \times 9.55 \times 293}{765 \times 6.25} K$$

T_2 = 219.5

T_2 = 219.5 – 273

= **–53.5°C**

19. Working at a vacuum line a chemist isolated a gas in weighing bulb with a volume of 255 cm^3 at a temperature of 25°C and under a pressure in the bulb of 10.0 torr. The gas weighed 12.1 mg. what was the formula mass of this gas?

Data:

Pressure of gas = 10 torr

$= \frac{10}{760} = 0.0132\text{atm}$

Volume of gas = 255 cm^3 = 0.255 dm^3
Temperature of gas = 25°C
= 25°C + 273 = 298 K
Mass of gas = 12.1 mg = 0.0121 g
General Gas Constant(R) = 0.0821 $dm^3atmK^{-1}mol^{-1}$

To Find: Formula mass (M) = ?

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

Solution: $M = \frac{WRT}{PV}$

$$M = \frac{0.0121g \times 0.0821dm^3\ atm\ K^{-1}\ mol^{-1}\ 298k}{0.0132\ atm \times 0.255dm^3}$$

$$= \frac{0.0121 \times 0.0821 \times 298}{0.0132\ atm \times 0.255}\ gmol^{-1}$$

$$M = \frac{0.296}{0.003366} = \mathbf{87.93\ gmol^{-1}}$$

20. What pressure is exerted by a mixture of 2.00g of H_2 and 8.00g of N_2 at 273K in a 10 dm^3 vessel?

Data:

Mass of H_2 = 2.00g

Mass of N_2 = 8.00 g

Temperature of mixture = 273K

Volume of the gas = $10dm^3$

To Find: Pressure of mixture of gases = ?

Formula: $PV = nRT$

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

Calculation of moles:

First of all convert masses of H_2 and N_2 into moles.

Number of moles of H_2 = $\frac{\text{Mass of } H_2}{\text{Molar mass of } H_2}$

Since, molar mass of H_2 = $2.00g\ mol^{-1}$

Putting the values

Number of moles of H_2 = $\frac{2.00}{2.00}$ = 1 mole

Mass of N_2 = 8.00g

Number of moles of N_2 = $\frac{\text{Mass of } N_2}{\text{Molar Mass of } N_2}$

Putting the values

Number of moles of N_2 = $\frac{8.00}{28}$ = 0.286

To calculate pressure of mixture of gases, we take total number of moles.

Total number of moles =1 + 0.286=**1.286**

Calculation of total pressure of gaseous mixture:

$$P = \frac{1.286 \text{ moles} \times 0.0821 dm^3 \text{ atm } K^{-1} mol^{-1} \times 273K}{10 dm^3}$$

$$= \frac{28.82}{10} \text{ atm} = \mathbf{2.88 \text{ atm}}$$

21. (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^3 of A will diffuse?

Data:

Density of gas A = 1.00

Density of gas B = 1.5

Volume of A diffused = 150 dm^3

To Find:

Volume of B disused = ?

Formula: $\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$

Solution: Volumes of gases differ correspond to the rates of diffusions.

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

Taking square on both sides

$$\frac{(150)^2}{r^2_B} = \frac{1.5}{1}$$

$$r^2_B = \frac{(150)^2}{1.5}$$

$$= 15000 \text{ dm}^6$$

$$r_B = \sqrt{15000}$$

$$= \mathbf{122.47 dm^3}$$

(b) Hydrogen (H_2) diffuses through a porous plate at a rate of 500 cm^3 per minute at 0^oC. What is the rate of diffusion of oxygen through the same porous plate of 0^oC.

Data:

Rate of diffusion of H_2 at 0^oC = $500 cm^3 min^{-1}$

To Find: Rate of diffusion O_2 at 0^oC = ?

Formula: $\frac{r_{O2}}{r_{H2}} = \sqrt{\frac{M_{H2}}{M_{O2}}}$

Molar mass of H_2 = 2 g mol^{-1}

Molar mass of O_2 = 32 g mol^{-1}

$$\frac{r_{O_2}}{500} = \sqrt{\frac{2}{32}}$$

$$\frac{r_{O_2}}{500} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$r_{O_2} = \frac{500}{4} = \mathbf{125 \text{ cm}^3 \text{ min}^{-1}}$$

So the rate of diffusion of O_2 is 125 cm^3/min

(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 H_2 gas through the same pinhole. Calculate the molecular mass of the unknown gas at S.T.P.

Data:

Rate of effusion of H_2 = 1

Rate of effusion of A = 0.279

To Find: Molar Mass of A = ?

Formula: $\frac{r_{H_2}}{R_A} = \sqrt{\frac{M_A}{M_{H2}}}$

Solution: Taking square on both sides

$$\left(\frac{1}{0.279}\right)^2 = \frac{M_A}{2}$$

$$M_A = \frac{2}{0.0778}$$

$$= \mathbf{25.7\ gmol^{-1}}$$

22. Calculate the number of molecules and the number of atoms in given amount of each gas.

(a) 20 cm³ of CH_4 at 0°C and pressure of 700 mm of mercury(Hg)

Data:

Volume of CH_4 = $20cm^3$

Volume of CH_4 = $0.02dm^3$

Temperature of CH_4 = 0^oC

= $0^oC + 273$ K = 273 K

Pressure of CH_4 = 700 mm Hg

= $\frac{700}{760}$ = 0.92 atm

General Gas Constant (R) = $0.0821\ dm^3 atm\ K^{-1}\ mol^{-1}$

To Find: Number of moles of CH_4= ?

Formula: PV = nRT

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

$$n = \frac{0.92atm \times 0.02dm^3}{0.0821dm^3\ atm\ K^{-1}\ mol^{-1} \times 273K}$$

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

$$n = \frac{0.0184}{22.356}\ moles$$

n = 8.2×10^{-4} moles of CH_4

Number of molecules of CH_4= $8.2 \times 10^{-4} \times 6.02 \times 10^{23}$

= 49.36×10^{19}

= $\mathbf{4.936 \times 10^{20}}$

One molecule of CH_4 has number of atoms = 5

Number of atoms inCH_4= $5 \times 4.936 \times 10^{20}$

= $\mathbf{2.47 \times 10^{21}}$**atoms**

(b) 1 ml of NH_3 at 100°C and pressure of 1.5 atm

Data: Volume of NH_3 = 1 ml

= 1ml = 1 cm^3 = 0.001 dm^3

Temperature of NH_3 = 100^oC

= $100^oC + 273 = 373$ K

Pressure of NH_3 = 1.5 atm

General Gas Constant (R) = 0.0821 $dm^3 atm. K^{-1} mol^{-1}$

To Find: Number of moles of NH_3 = ?

Formula: $PV = nRT$

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

Calculation of moles

$$n = \frac{1.5 atm \times 0.001\ dm^3}{0.0821\ dm^3\ atm.\ K^{-1}\ mol^{-1} \times 373K}$$

$$= \frac{1.5 \times 0.001}{30.62} \text{ moles}$$

$$= 4.89 \times 10^{-5} \text{ moles}$$

Calculation of number of molecules and number of atoms

Number of molecules of

NH_3 = moles × N_A

= $4.89 \times 10^{-5} \times 6.02 \times 10^{23}$

= **2.95×10^{19} molecules**

One molecule of NH_3 has number of atoms =4

2.94×10^{19} molecules have number of atoms

= $4 \times 2.943 \times 10^{19}$

= **1.179×10^{20} atoms**

23. Calculate the masses of 10^{20} molecules of each H_2, O_2 and CO_2 at S.T.P what will happen to the masses of these gases, when the temperature of the gases are increased by 100^oC and the pressure is decreased by 100 mm of Hg.

Data:

Molecules of H_2 = 10^{20}

Molecules of O_2 = 10^{20}

Molecules of CO_2 = 10^{20}

Increase of temperature= 100^oC

Increase of pressure = 100 mm of Hg

Molar mass of H_2 = 2g mol^{-1}

Mass of H_2 = ?

Mass of O_2 = ?

Mass of CO_2 = ?

Mass of H_2 molecules $= \frac{\text{Molar mass} \times \text{number of molecules of } H_2}{N_A}$

Since 1 mole of H_2 at S.T.P has number of molecules = 6.02×10^{23}

6.02×10^{23} molecules of H_2 at S.T.P. have Mass = 2.00g

Mass of H_2 molecules at S.T.P $= \frac{2}{6.02 \times 10^{23}} \times 10^{20}$

Mass of H_2 molecules at S.T.P $= \frac{2}{6.02} \times 10^{-3} =$ **3.3×10^{-4} g**

Molar mass O_2 = 32 $gmol^{-1}$

Mass of O_2molecules $= \frac{\text{Molar mass} \times \text{number of molecules of } O_2}{N_A}$

Mass of 10^{20} molecules of O_2 at S.T.P$=\frac{32}{6.02\times10^{23}} \times 10^{20}$g

$=$ **5.31×10^{-3}g**

Molar mass of CO_2 = 44 g mol^{-1}

Mass of CO_2 molecules $= \frac{\text{Molar mass} \times \text{number of molecules of } CO_2}{N_A}$

Mass of 10^{20} molecules of CO_2 at S.T.P $= \frac{44}{6.02\times10^{23}} \times10^{20}$

$=$ **7.30×10^{-3} g**

The change of temperature and pressure does not affect the masses because mass can neither be created nor bedestroyed so it remains constant.

24. Two moles of NH_3 are enclosed in a $5dm^3$ flask at 27^oC

(a) Calculate the pressure exerted by the gas assuming that

i. Gas behaves like an ideal gas

Data:
Volume = V = $5dm^3$
Temperature = T = 27^oC
= 27^o + 273 = 300K
Number of moles = n = 2 moles
General gas constant = R = 0.0821 atm.dm^3. $mol^{-1}K^{-1}$
To Find: Pressure = P = ?
Formula: PV = nRT
Solution:

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

$$P = \frac{2 \times 0.0821 \times 300}{5}$$

P = 9.852 atm

ii. Gas behaves like a real gas (a= 4.17 atmdm^6 mol^{-2} , b= 0.0371 dm^3mol^{-1})

Data:
Volume = V = $5dm^3$
Temperature = T = 27^oC
= 27^o + 273 = 300K
Number of moles = n = 2 moles
General gas constant = R = 0.0821 atm.dm^3. $mol^{-1}K^{-1}$
a= 4.17 atmdm^6 mol^{-2}
b= 0.0371 dm^3mol^{-1}
To Find: Pressure = P = ?
Formula: According to Van der waal's equation

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

Solution: $\left(P + \frac{an^2}{V^2}\right) = \frac{nRT}{(V-nb)}$

$$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

Putting the values

$$P = \frac{2 \times (0.0821) \times 300}{5 - 2 \times (0.0371)} - \frac{4.17 \times 2^2}{5^2}$$

$$P = \frac{49.26}{4.926} - \frac{16.68}{25}$$

$P = 10 - 0.67$ = 9.33 atm

(b) Also calculate the amount of pressure lessened due to forces of attraction at these conditions of volume and temperature

Amount of pressure lessened = 9.85 – 9.33 = 0.52 atm

Important long questions from past papers

1. State Charles's law. Explain its experimental verification.
2. Describe Dalton's law of partial pressures. Write its three applications.
3. State and explain Graham's law of diffusion of gases.
4. State Joule-Thomson effect. Explain Linde's method of liquefaction.
5. How pressure and volume were corrected by Van der Waal?
6. Derive Boyle's law and Charles' law from kinetic equation of gases.
7. Give postulates of Kinetic Molecular Theory of Gases.
8. Example# 3, 4, 5, 7, 8