

3. GASEOUS STATE

1. INTRODUCTION

1.1 States of Matter

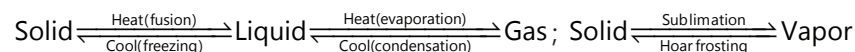
Matter can be defined as anything that occupies volume and has mass. Matter can be classified into three states – solid, liquid and gas. Plasma is regarded as the fourth state of matter, which exists only at very high temperatures (at interiors of stars, 10⁷ K). At very high temperatures, all gases become ionized, which results in the formation of the fourth state of matter, the so-called plasma state.

A solid state has definite shape and volume at a given temperature and pressure. A liquid has definite volume but no definite shape, whereas a gas has neither definite volume nor definite shape.

A substance can exist in either of the three states depending on the temperature and pressure under which it exists, e.g. at ordinary temperature and pressure, water exists as liquid and can be passed into gaseous state at 100°C. A substance can also exist in all the three states simultaneously, e.g. water has all the three phases in equilibrium at 4.58 mm Hg pressure and 0.0098°C, which is known as triple point, i.e. the point at which three phases of a component exist together.



Thus, an increase in the forces of attraction (by increasing pressure) and a decrease in the kinetic energy (by lowering temperature) may result in the conversion of the gaseous state into the liquid state and then into the solid state. Different states of matter are thus, associated with definite energy contents and are interconvertible.



1.2 The Gaseous State

Measurable Properties of Gases

- Mass:** The amount of a gas is expressed in terms of its number of moles. For a gas with a molar mass M , the mass in gram (w) is related to the number of moles (n) as $n = w/M$
- Volume:** The volume of a gas is the space occupied by its molecules under a given set of conditions. Volume of the container in which a gas is enclosed is expressed as $1 \text{ m}^3 = 10^3 \text{ L} = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3$
- Temperature:** The extent of hotness or coldness of a body is known as temperature. The measurement of temperature is based on the principle that substances expand on heating.

The units used for the measurement of temperature are as follows:

- (i) Centigrade or Celsius scale (named after Anders Celsius)
- (ii) Fahrenheit scale (named after Daniel Fahrenheit, a German instrument maker)
- (iii) Kelvin scale (name after Lord Kelvin). Also, $K = ^\circ\text{C} + 273.15$

The Celsius and Fahrenheit scales are related by the following: $\frac{F - 32}{9} = \frac{C}{5}$

$0^\circ\text{C} = 32^\circ\text{F}$ and $37^\circ\text{C} = 98.6^\circ\text{F}$ (human body temperature)

- (d) **Pressure:** The force experienced by the walls of a container due to the bombardment of gas molecules. This force per unit area of the walls is known as gas pressure.

The pressure of pure gas is measured by manometer while that of mixture of gas is measured using barometer.

A standard or normal atmospheric pressure is the pressure exerted by a mercury

column of exactly 76 cm at 0°C , which is the pressure exerted by the atmosphere at the sea level.

The smaller unit commonly used for expressing the pressure of a gas is mm or torr

(after the name of Torricelli, who invented the barometer). Thus,

$$1 \text{ atm} = 76 \text{ cm} = 760 \text{ mm or } 760 \text{ torr}$$

The unit of pressure commonly used is 'bar.'

$$1 \text{ atm} = 1.01325 \text{ bar or } 1 \text{ bar} = 0.987 \text{ atm}$$

The SI unit of pressure is pascal (Pa). Pa is defined as the pressure exerted by a force of 1 newton on an area of 1 m^2 .

$$1 \text{ Pa} = 1 \text{ Nm}^{-2} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$$

1.3 Atmosphere and Atmospheric Pressure

A thick blanket of air that surrounds the earth is called atmosphere. Molecules of various gases that are present in the atmosphere are under constant pull of the gravitational force of the earth. As a result of this, the atmosphere is dense near the surface of the earth than that at high altitudes. Force experienced by molecules in any area of the earth exposed to the atmosphere is equal to the weight of the column of the air above it. This force per unit area of the earth is known as atmospheric pressure.

$$1 \text{ atm} = 76.0 \text{ cm of mercury} = 760 \text{ mm of mercury} = 760 \text{ torr} = 1.01325 \times 10^5 \text{ Pa}$$

MASTERJEE CONCEPTS

The high density of mercury (13.6 g/mL) leads to shorter length of glass tube. The closed-end manometer should not contain water droplets adhered inside its long arm. If it is so, the observed pressure would be lower than the real pressure exerted by the gas.

The figure below shows a manometer and a barometer. A barometer is used to measure atmospheric pressure. The basic concept used in all pressure-measuring instruments is given below:

$$P_A = P_B + \rho g \Delta h, \text{ where } \Delta h \text{ is the height difference between the points A and B}$$

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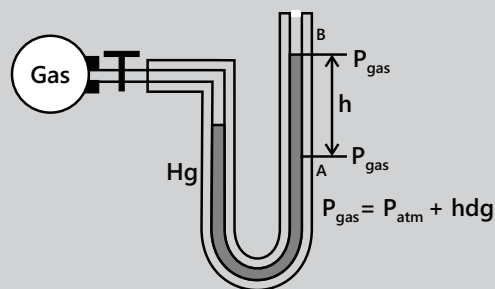


Figure 3.1: An open arm manometer

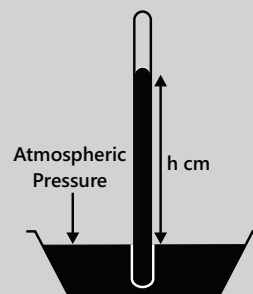


Figure 3.2: Barometer

Things to Remember:

| Name | Symbol | Value |
|------------------------|--------|--|
| Pascal | 1 Pa | 1 Nm^{-2} , $1 \text{ kg m}^{-1}\text{s}^{-2}$ |
| Bar | 1 bar | 10^5 Pa |
| Atmosphere | 1 atm | 101.325 kPa |
| Torr | 1 torr | $101\,325/760 \text{ Pa} = 133.32 \text{ Pa}$ |
| Millimeters of mercury | 1 mmHg | 133.322 Pa |
| Pound per square inch | 1 psi | 6.894 757 kPa |

The pressure is independent of the shape and cross-sectional area of the column. The mass of the column of a given height increases as the area, so does the area on which the force acts. Hence, the two cancel each other.

This difficulty can be solved by carrying oxygen cylinders.

STP conditions: 0°C or 273.15 K temperature and 1 atm ($=1.01325 \text{ bar}$) pressure

Standard Ambient Temperature and Pressure (SATP)

SATP conditions: 298.15 K (25°C) and 1 bar (10^5 Pa) pressure

The molar volume of an ideal gas at SATP conditions is $24.789 \text{ L mol}^{-1}$.

Saurabh Gupta (JEE 2010, AIR 443)

2. GAS LAWS

Among the three common states of matter, the gaseous state is the simplest. The laws of gaseous behavior are more uniform and better understood. The well-known laws of gaseous behavior are the Boyle's law, Charles's law, Graham's law and Avogadro's law.

2.1 Boyle's Law

Boyle's law states that at constant temperature, the volume of a given mass of a gas is inversely proportional to pressure.

$$V \propto \frac{1}{P} \quad (T \text{ and mass of gas constant}); \quad PV = \text{constant}$$

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

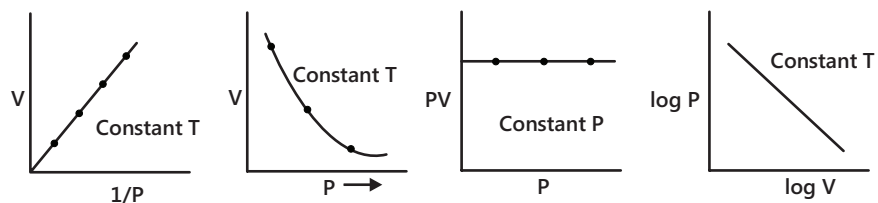


Figure 3.3: Various plots of pressure (P) vs Volume (V)

2.2 Charles's Law

Charles's law states that at constant pressure, the volume of a given mass of gas is directly proportional to its absolute temperature, i.e. $V \propto T$ (P and m constant) $\Rightarrow V = KT \Rightarrow \frac{V}{T} = \text{constant} = K$

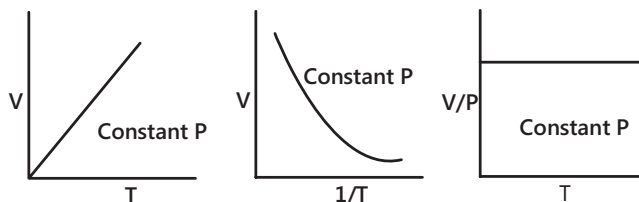


Figure 3.4: Various plot of volume (V) vs Temperature (T)

2.3 Gay-Lussac's Law or Pressure-Temperature Law

Gay-Lussac's law states that at constant volume, the pressure of a given mass of gas is directly proportional to its absolute temperature, i.e. $P \propto T$ (V and mass of gas constant).

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

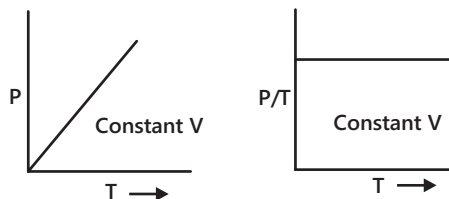


Figure 3.5: Plots of pressure (P) vs Temperature (T)

2.4 Avogadro's Law

Avogadro's law states that equal volumes of all gases under similar conditions of temperature and pressure will contain equal number of molecules or vice versa, i.e. $V \propto n$ (at constant T and P)

MASTERJEE CONCEPTS

- To test the validity of a relation between two quantities, it is best to plot them in such a way that they should give a straight line since deviations from a straight line are much easier to detect than deviations from a curve. The following are the various curves that show the variation with increasing P , V and T :

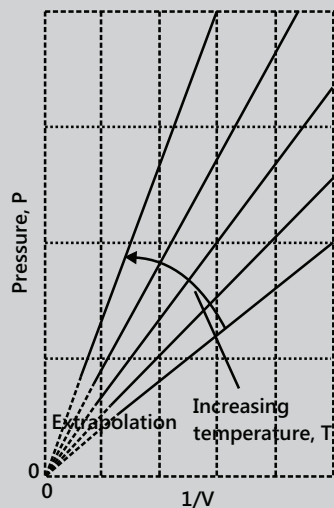


Figure 3.6 (a): Straight lines are obtained when the pressure is plotted against $1/V$ at constant temperature

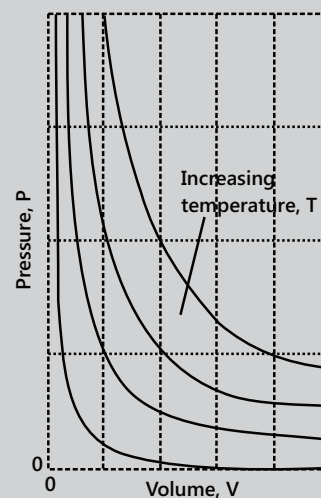


Figure 3.6 (b): The pressure-volume dependence of a fixed amount of perfect gas at different temperatures. Each curve is a hyperbola ($pV = \text{constant}$) and is called an isotherm

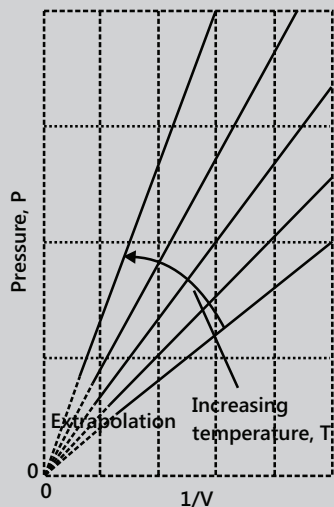


Figure 3.6 (c): The pressure also varies linearly with the temperature at constant volume and extrapolates to zero at $T = 0$ (-273°C)

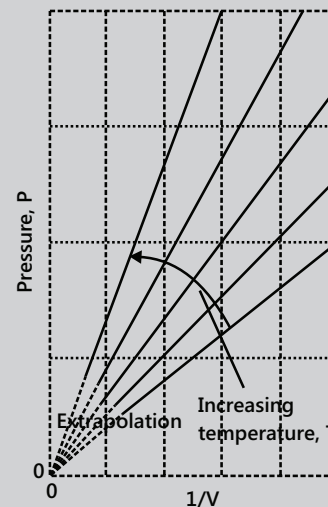


Figure 3.6 (d): The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at $T = 0$ or $\theta = -273^\circ\text{C}$

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An automobile tire is inflated to lessen the pressure in summer because in summer the pressure of the gas inside a tire increases due to an increase in temperature.

A contraction in the volume of a gas-filled balloon is noticed in night because of relatively low temperature in night.

- Combined Gas Law: $\frac{PV}{T} = \text{Constant} \Rightarrow \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$
- At a higher pressure, gases deviate from Boyle's law and a straight line is not obtained.

Neeraj Toshniwal (JEE 2009, AIR 21)

3. IDEAL GAS EQUATION

From the gas laws, we have found that $V \propto \frac{1}{P}$ (Boyle's law); $V \propto T$ (Charles's law); $V \propto n$ (Avogadro's law); and $V \propto \frac{nT}{P} \Rightarrow PV = nRT$, where R = universal gas constant.

Hence, $PV = nRT$ is the ideal gas equation.

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

At STP, for 1 mole of gas

$P = 1 \text{ atm}$; $V = 22.4 \text{ L}$; $T = 273 \text{ K}$; $n = 1 \text{ mole}$

$$\Rightarrow R = \frac{1 \times 22.4}{1 \times 273} = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$R = \frac{(76 \times 13.6 \times 981)22400}{1 \times 273} = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}; R = 1.99 \text{ cal K}^{-1} \text{ mol}^{-1}$$

3.1 Relation of Density with Ideal Gas Equation

$$PV = nRT; N = \text{Number of moles} = \frac{\text{amount of gas}}{\text{Mol. wt of gas}} = \frac{w}{M_0}$$

$$\Rightarrow PV = \frac{w}{M_0} \times RT \Rightarrow PM_0 = \frac{w}{V} RT = DRT, \text{ where } D = \text{Density of gas}; PM_0 = DRT$$

MASTERJEE CONCEPTS

Boyle's law states that at constant temperature, if pressure on a gas increases, the gas volume decreases and vice versa. But when air is filled in a balloon, both volume and pressure increase. Why?

Ans. The law is applicable only for a definite mass of gas. As air is filled in the balloon, more and more air is introduced in the balloon. Thus, the mass of the air present inside is increased and the number of moles are also increased. Hence, the law is not applicable.

The size of a weather balloon keeps on becoming big as it rises to a higher altitude because at a higher altitude the external pressure (i.e. atmospheric pressure) on the balloon goes on

Fact: Decreasing and thus the size of the balloons increases. On pushing or blowing air in a balloon, its pressure and volume

Fact: Increase due to an increase in energy. The product of PV has dimension in number of moles.

$$P \times V = \frac{\text{force}}{\text{area}} \times \text{area} \times \text{length} = \text{force} \times \text{length} = \text{work} = \text{energy}$$

Note: Physical significance of R. For 1 mole of a gas

$$R = \frac{PV}{T} = \frac{(\text{Force} / \text{Area})(\text{Area} \times \text{Length})}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}} = \frac{\text{Work done}}{\text{Temperature change}}$$

Note: Thus 'R' represents work done per degree per mole of the gas.

Saurabh Chaterjee (JEE Advanced 2013, AIR)

Illustration 1: A spherical balloon having a diameter of 21 cm is to be filled up with H_2 at NTP from a cylinder containing the gas at 20 atm at 27°C . The cylinder can hold 2.82 L of water at NTP. Find out the number of balloons that can be filled up. **(JEE Advanced)**

Sol: Volume of one balloon (to be filled)

$$= \left(\frac{4}{3}\right) \pi r^3 = \left(\frac{4}{3}\right) \times \left(\frac{22}{7}\right) \times \left(\frac{21}{2}\right)^3 = 4851 \text{ mL} = 4.851 \text{ L}$$

Let 'n' balloons are filled, then the total volume of H_2 used in filling the balloons = $4.851 \times n$ L. After n balloons are filled, the cylinder of H_2 used in filling the balloons will also have H_2 in it.

Volume of the cylinder = 2.82 L

λ The total volume of H_2 at NTP = Volume of 'n' balloons + volume of the cylinder

$$= 4.851 \times n + 2.82 \quad \dots \text{(i)}$$

The volume of available H_2 at NTP can be derived by the following data:

$$P = 1 \text{ atm}, \quad V = ? \quad T = 273 \text{ K} \quad \text{And} \quad P = 20 \text{ atm}, \quad V = 2.82 \text{ L}, \quad T = 300 \text{ K}$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad \frac{1 \times V}{273} = \frac{20 \times 2.82}{300} = 51.32$$

$$\Rightarrow V = \frac{20 \times 2.82 \times 273}{300} = 51.32 \quad \dots \text{(ii)}$$

From equations (i) and (ii), we find that both are same

$$\therefore 4.851 \times n + 2.82 = 51.32$$

$$\Rightarrow n = 10$$

Illustration 2: A car tire has a volume of 10 L when inflated. At 17°C, the tire is inflated to a pressure of 3 atm with air. As a result of driving, the temperature of the tire increases to 47°C.

(a) At this temperature, what would be the pressure?

(b) How many liters of air measured at 47°C and pressure of 1 atm should be allowed to let out to restore the tire to 3 atm at 47°C? **(JEE MAIN)**

Sol: The pressure-volume relation is an inverse one while the change with the temperature is a direct.

Initial volume of tire = 10 L, P = 3 atm, T = 290 K

After driving, the volume of the tire = 10 L, P = ?, T = 320 K

(a) At constant volume, $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{3}{290} = \frac{P}{320} \Rightarrow P = 3.31 \text{ atm}$

(b) To have a pressure of 3.0 atm inside the tire at 320 K, the decrease in pressure should be $3.31 - 3.0 = 0.31 \text{ atm}$ at 320 K

This amount of pressure has a volume of 10 L. Thus, the volume of gas taken out at 1 atm and 320 K is obtained by using the equation $P_1V_1 = P_2V_2$

$$0.31 \times 10 = 1 \times V \Rightarrow V = 3.1 \text{ L}$$

Illustration 3: Mercury diffusion pumps may be used in laboratory to produce a high vacuum. Generally, cold traps are placed between the pump and the system to be evacuated, which results in condensation of mercury vapor and prevent mercury from diffusing back into the system. The minimum pressure of mercury that can exist in the system is the vapor pressure of mercury at the temperature of the cold trap. Find out the number of mercury atoms per unit volume in a cold trap at -120°C . The vapor pressure of mercury at this temperature is given as 10^{-16} torr. **(JEE MAIN)**

Sol: The no. of moles are calculated by using ideal gas equation which when multiplied by the Avogadro's number gives the number of atoms.

Given, P = 10^{-16} mm, V = 1 L, T = $273 - 120 = 153 \text{ K}$

$$\therefore PV = nRT$$

$$\therefore n = \frac{PV}{RT} = \frac{10^{-16} \times 1}{760 \times 0.0821 \times 153} = 1.047 \times 10^{-20}$$

$$\therefore \text{Number of mercury atoms} = 6.023 \times 10^{23} \times 1.047 \times 10^{-20} = 6306 \text{ atoms/L}$$

Illustration 4: An underwater bubble having a radius of 0.5 cm at the bottom of a tank, where the temperature is 5°C and pressure is 3 atm, rises to the surface, where the temperature is 25°C and pressure is 1 atm. What will be the radius of the bubble when it reaches to the surface? **(JEE MAIN)**

Sol: Considering the water bubble as a sphere and equating the two conditions with the help of ideal gas equation, the radius can be calculated.

The moles of air contained in bubble at the bottom of the tank as well as on the surface remain same.

$$\therefore n = \frac{P_1V_1}{RT_1} = \frac{P_2V_2}{RT_2}$$

$$\text{At bottom of the tank or at the surface } \frac{3 \times (4/3)\pi \times (0.5)^3}{R \times 278} = \frac{1 \times (4/3)\pi r^3}{R \times 298} \therefore r = 0.74 \text{ cm}$$

4. DALTON'S LAW OF PARTIAL PRESSURES

Statement: At a given temperature, the total pressure exerted by two or more non reacting gases occupying a definite volume is equal to the sum of the partial pressures of component gases.

$$P_{\text{Total}} = \frac{(n_{\text{Total}} RT)}{V}$$

Let n_A moles of A, n_B moles of B, etc., be the non-reacting gases present in a container of volume V at a constant temperature.

$$P_T = \frac{(n_A + n_B + n_C + n_D + \dots)RT}{V} = \frac{(n_A RT)}{V} + \frac{n_B RT}{V} + \frac{n_C RT}{V} + \frac{n_D RT}{V} + \dots = P_A + P_B + P_C + P_D + \dots$$

Where P_A , P_B , etc., are the partial pressures of individual gases if they were present alone in the same container of volume V (liters) and same constant temperature T .

The partial pressures can be calculated as follows:

P_A is also equal to the mole fraction of a gas multiplied by the total pressure exerted by the mixture of gases.

$$P_A = \frac{n_A}{n} \times P_T = X_{AP} T, \text{ where } X_A = \text{Mole fraction of a gas}$$

4.1 Applications of Dalton's Law of Partial Pressures

(i) In the determination of pressure of a dry gas:

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

If P and P' are the pressures of the moist and dry gases, respectively, at $t^\circ\text{C}$ and p is the aqueous tension at that temperature, then according to Dalton's law of partial pressures

$$P = P' + p \text{ or } P' = P - p, \text{ i.e. } P_{\text{dry gas}} = P_{\text{moist gas}} - \text{aqueous tension (at } t^\circ\text{C)}$$

MASTERJEE CONCEPTS

If a gas is collected over a liquid, it must be borne in mind that its pressure is partial, which is equal to the difference between the total pressure of the gas mixture and the partial pressure of the vapor of the liquid.

Pressures of moist gas = Pressure of dry gas + pressure of water vapor, $P_{\text{moist}} = P_{\text{dry gas}} + P_{\text{H}_2\text{O vapor}}$
(Since $P_{\text{moist gas}} > P_{\text{Dry gas}}$)

Dalton's Law is also applicable for a gaseous system at equilibrium.

Fact: Saturated vapor does not obey gas laws, except Dalton's law, as its pressure is independent of volume. It has been found that aqueous tension depends only on temperature.

Aman Gour (JEE 2012, AIR 11)

4.2 Relative Humidity

The relative humidity (RH) can be defined as the ratio of the mass of water vapors (m) actually present in a certain volume of air at room temperature to the maximum mass of water vapors (M) required to saturate the same volume of air at the same temperature, i.e.

$$\text{Relative humidity (RH)} = \frac{m}{M}$$

As vapor pressure of water at a constant volume and temperature is proportional to its mass $\left[PV = \frac{w}{m}RT \therefore P \propto w \right]$, therefore

$$(RH) = \frac{\text{Vapour pressure of water at room temperature in air (or gas)}}{\text{Saturated vapour pressure at room temperature in air (or gas)}}$$

MASTERJEE CONCEPTS

At dew point, a gas becomes saturated so that the vapor pressure of H_2O at room temperature is equal to the saturated vapor pressure of water at dew point.

$$RH = \frac{\text{Saturated vapor pressure at dew point}}{\text{Saturated vapor pressure at room temperature}}$$

Rohit Kumar (JEE 2012, AIR 79)

Illustration 5: In a 1-L flask, 250 mL of nitrogen maintained at 720 mm pressure and 380 mL of oxygen maintained at 650 mm pressure are put together. If the temperature is kept constant, then what will be the final pressure of the mixture?

Sol: Step 1- Calculation of the partial pressure of nitrogen

| Given conditions | Final conditions |
|-------------------------|------------------|
| Volume $V_1 = 250$ mL | $V_2 = 1000$ mL |
| Pressure $P_1 = 720$ mm | $P_2 = ?$ mm |

Applying Boyle's Law (since the temperature remains constant), we get

$$P_2V_2 = V_1P_1, \text{ i.e. } 1000 \times P_2 = 720 \times 250 \text{ or } P_2 = \frac{720 \times 250}{1000} = 180 \text{ mm}$$

Hence, the partial pressure due to nitrogen (P_{N_2}) = 180 mm

Step 2- Calculation of the partial pressure of oxygen

| Given conditions | Final conditions |
|------------------|------------------|
| $V_1 = 380$ mL | $V_2 = 1000$ mL |
| $P_1 = 650$ mm | $P_2 = ?$ mm |

Applying Boyle's Law (since the temperature remains constant), we get

$$P_2V_2 = V_1P_1, \text{ i.e., } 1000 \times P_2 = 380 \times 650 \text{ or } P_2 = \frac{380 \times 650}{1000} = 247 \text{ mm}$$

Hence, the partial pressure due to oxygen (P_{O_2}) = 247 mm

Step 3- Calculation of the final pressure of the gaseous mixture

If P is the final pressure of the gaseous mixture, then by Dalton's law of partial pressure

$$P = P_{N_2} + P_{O_2} = 180 + 247 = 427 \text{ mm}$$

Illustration 6: The volume occupied by a given mass of a gas is 919.0 mL in dry state at STP. The same mass when collected over water at 15°C and 750 mm pressure occupies a volume of 1 L. Find out the vapor pressure of water at 15°C. **(JEE MAIN)**

Sol: Step 1- Calculation of the pressure of the dry gas at 15°C and 750 mm pressure

Given conditions at STP

Final conditions

$$V_1 = 919 \text{ mL}$$

$$V_2 = 1000 \text{ mL}$$

$$P_1 = 760 \text{ mm}$$

$$P_2 = ? \text{ (Dry state)}$$

$$T_1 = 273 \text{ K,}$$

$$T_2 = 273 + 15 = 288 \text{ K}$$

By applying gas equation, we get

$$\frac{760 \times 919}{273} = \frac{P_2 \times 1000}{288} \text{ or } P_2 = \frac{760 \times 919 \times 288}{1000 \times 273} \text{ mm}$$

Step 2- Calculation of the vapor pressure of water at 15°C

Vapor pressure of water = Pressure of the moist gas – pressure of the dry gas
= 750 – 736.7 = 13.3 mm

Alternatively, if P is the vapor pressure of water at 15°C, take $P_2 = (750 - p)$ mm

Substituting in the equation $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$, we get $\frac{760 \times 919}{273} = \frac{(750 - p) \times 1000}{288}$

Solve for p.

Illustration 7: The density of a mixture of O₂ and N₂ at NTP is given as 1.3g/L. Calculate the partial pressure of O₂. **(JEE ADVANCED)**

Sol: Let n_1 and n_2 be the moles of O₂ and N₂, respectively, in the mixture

$$\therefore \text{Average molecular weight of the mixture (m)} = \frac{32 \times n_1 + 28 \times n_2}{n_1 + n_2} \quad \dots \text{ (i)}$$

$$\text{For mixture: } PV = (w/m)RT \text{ or } m = \frac{w}{VP} \cdot RT = \frac{1.3 \times 0.0821 \times 273}{1} \quad \dots \text{ (ii)}$$

$$m = 29.137$$

By using equations (i) and (ii), we get

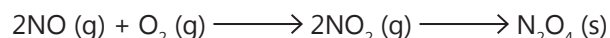
$$\frac{32n_1 + 28n_2}{n_1 + n_2} = 29.137$$

$$\therefore \frac{28n_1 + 28n_2 + 4n_1}{n_1 + n_2} = 29.137$$

$$\text{or } \frac{4n_1}{n_1 + n_2} = 29.137 - 28 \text{ or } \frac{n_1}{n_1 + n_2} = 0.28, \text{ i.e. mole fraction of O}_2 = 0.28$$

Now, $P'_{O_2} = PM \times \text{mole fraction of O}_2 = 1 \times 0.28 = 0.28 \text{ atm}$

Illustration 8: At room temperature, the following reaction goes to completion.



The dimer N₂O₄ at 262 K is solid. A stopcock separates a 250-mL flask and a 100-mL flask. At 300 K, a pressure of 1.053 atm is exerted by the nitric oxide in the larger flask and the smaller one contains O₂ at 0.789 atm. The gases

are mixed by opening the stopcock. After the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapor pressure of the dimer, calculate the pressure and composition of the gas remaining at 220 K. (Assume that the gases behave ideally.) **(JEE ADVANCED)**

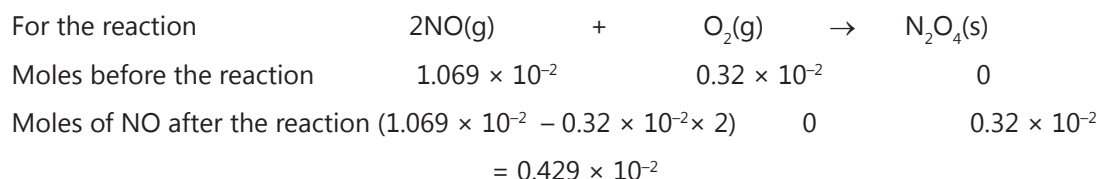
Sol: Using ideal gas equation, no. of moles is calculated for every reacting species and then the reaction with mole-concentration calculations is laid down.

For NO: $V = 250 \text{ mL}$, $T = 300 \text{ K}$, $P = 1.053 \text{ atm}$

$$\therefore n_{\text{NO}} = \frac{PV}{RT} = \frac{1.053 \times 250}{0.0821 \times 300 \times 1000} = 1.069 \times 10^{-2}$$

For O_2 : $V = 100 \text{ mL}$, $T = 300 \text{ K}$, $P = 0.789$

$$\therefore n_{\text{O}_2} = \frac{PV}{RT} = \frac{0.789 \times 100}{0.0821 \times 300 \times 1000} = 0.32 \times 10^{-2}$$



∴ The gas left is NO, which is

$$= 4.29 \times 10^{-3} \text{ mol}$$

Moreover, $P \times V = nRT$

$$\text{At } T = 220 \text{ K}, V = \frac{250 + 100}{1000} \text{ L} = 0.35 \text{ L}$$

$$P \times (0.35) = 4.29 \times 10^{-3} \times 0.0821 \times 220; P_{\text{NO}} = 0.221 \text{ atm}$$

5. DIFFUSION OF GASES AND GRAHAM'S LAW OF DIFFUSION

The rate of diffusion r for two gases under different pressures is given by: $\frac{r_1}{r_2} = \left(\sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \right)$
(at constant T) ... (i)

Further, the rate of diffusion (r) can be expressed in terms of:

$$r = \frac{\text{Volum diffused (V)}}{\text{Time taken}} = \frac{\text{Moles diffused (n)}}{\text{Time taken}} = \frac{\text{Distance travelled in a narrow tube (d)}}{\text{Time taken}}$$

Thus, according to Graham's law of diffusion at constant P and T

$$\frac{V_1}{t_1} \times \frac{t_2}{V_1} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}} \quad \dots \text{ (ii)}$$

Where V_1 and V_2 are the volumes diffused in time t_1 and t_2

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}} \quad \dots \text{ (iii)}$$

Where n_1 and n_2 are the moles diffused in time t_1 and t_2

$$\frac{d_1}{t_1} \times \frac{t_2}{d_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}} \quad \dots \text{ (iv)}$$

Where d_1 and d_2 are the distances traveled by molecules in a narrow tube in time t_1 and t_2

$$\text{or } \frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\frac{M_1}{M_2}} \quad \dots (v)$$

Where w_1 and w_2 are the weights diffused in time t_1 and t_2 .

Instantaneous rate of diffusion: During diffusion, the partial pressure of a component present in a mixture or the pressure of a gas decreases continuously due to a decrease in the number of moles. Therefore, instantaneous rate of diffusion may be expressed in terms of instantaneous decrease in the partial pressure of that component present

in the mixture or a decrease in the pressure of the gas, i.e. $-\frac{dP}{dt}$

$$\therefore -\frac{dP}{dt} \propto \frac{P}{\sqrt{M}} = \frac{KP}{\sqrt{M}} \text{ or } P_2 = P_1 e^{-\frac{Kt}{\sqrt{M}}}$$

i.e. pressure of a gas shows exponential decrease with time.

Barometric Distribution Law: The variation of pressure with altitude is given by Barometric formula.

$$P = P^\circ e^{-Mgh/RT}$$

Where P and P° are the pressure of the gas at the ground level and at a height 'h' from the ground respectively.

Since number of moles of gas 'n' and density of the gas 'd' are proportional to pressure hence the above equation may be expressed as

$$d = d^\circ e^{-Mgh/RT} \text{ and } n = n^\circ e^{-Mgh/RT}$$

The above equation may be expressed as,

$$\log \frac{P}{P^\circ} = \log \frac{d}{d^\circ} = \log \frac{n}{n^\circ} = \frac{1}{2.303} \times \frac{Mgh}{RT}$$

Illustration 9: A compound exists in the gaseous phase both as a monomer (A) and a dimer (A_2). The molecular weight of A is given as 48. In an experiment, 96 g of the compound was confined in a vessel having a volume 33.6 L and heated to 273°C . Find out the pressure developed if the compound exists as a dimer to the extent of 50% by weight under these conditions. **(JEE MAIN)**

Sol: Since A and A_2 are the two states in the gaseous phase having their weight ratio 50%, i.e. 1: 1

$$\text{Moles of } A = \frac{96}{2} \times \frac{1}{48} = 1 \quad \left(n = \frac{w}{m} \right)$$

$$\text{Moles of } A_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$$\therefore \text{Total moles of } A \text{ and } A_2 = 1 + \frac{1}{2} = \frac{3}{2}$$

Now, $PV = nRT$

$$\therefore P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546 \quad \therefore P = 2 \text{ atm}$$

Illustration 10: Pure O_2 diffuses through an aperture in 224 seconds, whereas a mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 seconds. Calculate the molecular weight of the gas. **(JEE MAIN)**

Sol: The gaseous mixture contains 80% O_2 and 20% another gas.

$$\therefore \text{The average molecular weight of the mixture } (M_m) = \frac{32 \times 80 + 20 \times m}{100} \quad \dots (i)$$

Now, for diffusion of the gaseous mixture and pure O₂

$$\frac{r_{O_2}}{r_m} = \sqrt{\frac{M_m}{M_{O_2}}} \text{ or } \frac{V_{O_2}}{V_m} \times \frac{t_m}{t_{O_2}} = \sqrt{\frac{M_m}{32}} \quad \text{or } \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_m}{32}}$$

$$\therefore M_m = 34.92 \quad \dots \text{ (ii)}$$

Using equations. (i) and (ii), we find that the molecular weight of the gas (m) = 46.6

Illustration 11: At 20°C, two balloons having equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg of N₂ and the other with 1 kg of H₂. The N₂ balloon leaks to a pressure of 1/2 atm in 1 h. How long would it take for the H₂ balloon to reach a pressure of 1/2 atm? **(JEE ADVANCED)**

Sol: Given for N₂: initially, P₁ = 2 atm w₁ = 14 kg (diffusion time 1 h)

$$\text{After diffusion, } P_2 = \frac{1}{2} \text{ atm, } w_2 = ?$$

Since for a gas at constant V and T, P ∝ w

$$\therefore \frac{P_1}{P_2} = \frac{w_1}{w_2} \text{ or } \frac{2}{1/2} = \frac{14}{w_2} \quad \therefore w_2 = \frac{14}{4} \text{ kg N}_2$$

$$\therefore \text{The weight of N}_2 \text{ diffused in 1 h} = 14 - (14/4) = (21/2) \text{ kg}$$

Similarly for H₂: initially P₁ = 2 atm, w₁ = 1 kg (diffusion time t h)

$$\text{After diffusion, } P_2 = \frac{1}{2} \text{ atm, } w_2 = ?$$

$$\text{Again, } \frac{P_1}{P_2} = \frac{w_1}{w_2} \text{ or } \frac{2}{1/2} = \frac{1}{w_2}; w_2 = \frac{1}{4} \text{ kg}$$

$$\therefore \text{The weight of H}_2 \text{ diffused} = 1 - \left(\frac{1}{4}\right) = \frac{3}{4} \text{ kg}$$

For diffusion of N₂ and H₂, t_{H₂} = 1 h = 60 min

$$\frac{w_{H_2}}{t_{H_2}} \times \frac{t_{N_2}}{w_{N_2}} = \sqrt{\frac{M_{H_2}}{M_{N_2}}}; \frac{(3/4)}{(21/2)} \times \frac{60}{t} = \sqrt{\frac{2}{28}}$$

$$t = 16 \text{ min}$$

Illustration 12: A mixture containing 2.24 L of H₂ and 1.12 L of D₂ at NTP is put inside a bulb connected to another bulb by a stopcock with a small opening. The second bulb has been fully evacuated. The stopcock is opened for a certain period of time and then cooled. Now the first bulb is found to contain 0.10 g of D₂. Calculate the % by weight of the gases in the second bulb. **(JEE ADVANCED)**

Sol: In bulb I before diffusion:

At STP, H₂ = 2.24 L = 0.2 g = 0.1 mole; D₂ = 1.12 L = 0.2 g = 0.05 mole

When these moles are placed inside the bulb, the partial pressures of the gases will be different because V and T are constant.

Also, P ∝ n

$$\therefore \frac{P_{D_2}}{P_{H_2}} = \frac{0.05}{0.10} = \frac{1}{2}$$

After diffusion, the amount of D_2 left = 0.1 g $\therefore D_2$ diffused in given time = 0.2 – 0.1 g = 0.1 g

Hence, for diffusion of H_2 and D_2

$$\frac{w_{H_2}}{t_{H_2}} \times \frac{t_{D_2}}{w_{D_2}} = \sqrt{\frac{M_{H_2}}{M_{D_2}}} \times \frac{P_{H_2}}{P_{D_2}}$$

\therefore Time taken is same

$$\frac{w_{H_2}}{0.10} = \sqrt{\frac{2}{4}} \times 2 \quad \therefore w_{H_2} = 0.10 \times \sqrt{2} = 0.14 \text{ g}$$

\therefore Weight of gases in bulb II = Weight of D_2 + Weight of H_2 = 0.10 + 0.14 = 0.24 g

\therefore % D_2 by weight = (0.10/0.24) = 41.66%

6. KINETIC THEORY OF GASES

The kinetic theory of gases (proposed by Bernoulli in 1738; developed by Clausius, Maxwell and Boltzmann) postulates the following:

- (a) Gaseous molecules are considered to be point masses.
- (b) The volume of a molecule of a gas is negligible as compared with the total volume of the gas.
- (c) Gaseous molecules do not have appreciable attraction; hence, gases can be easily compressed and do not have fixed shape and volume.
- (d) Gaseous molecules collide with each other but their collisions are perfectly elastic, i.e. there is no net loss of energy.

Consider two molecules A and B with mass m . Their speeds are V_A and V_B , respectively. After collision, let the new speeds to be $V_{A'}$ and $V_{B'}$, respectively. As the collisions are perfectly elastic,

Total energy before collision – Total energy after collision

$$\frac{1}{2}MV_A^2 + \frac{1}{2}MV_B^2 = \frac{1}{2}MV_{A'}^2 + \frac{1}{2}MV_{B'}^2 \Rightarrow V_A^2 + V_B^2 = V_{A'}^2 + V_{B'}^2$$

- (e) The average kinetic energy of a molecule is directly proportional to its temperature.
- (f) There is no effect of gravity on the molecular motion.
- (g) The pressure exerted is due to collisions with the wall of the container.

7. KINETIC ENERGY AND MOLECULAR SPEEDS

Kinetic Gas Equation

The equation $\Rightarrow PV = \frac{1}{3} mnc^2$ is known as the kinetic gas equation.

For 1 mole of a gas, $n = 6.023 \times 10^{23} = Na$

$$\Rightarrow n \times m = m \times Na = 6.023 \times 10^{23} \times m = M \Rightarrow PV = \frac{1}{3} Mc^2 \text{ for 1 mole of a gas.}$$

Kinetic Energy and temperature: suppose 1 mole of a gas is under consideration, the number of molecules involved will then be n_A . Then, according to the kinetic gas equation

$$PV = \frac{1}{3} mnc^2; PV = \frac{1}{3} mnc^2 \text{ for 1 mole of gas}$$

$$\Rightarrow PV = RT \Rightarrow RT = \frac{1}{3} M_0c^2 \Rightarrow RT = \frac{2}{3} \times \left(\frac{1}{2} M_0c^2 \right) = \frac{2}{3} \times \text{KE}$$

Where KE = Kinetic energy per mole of $\frac{2}{3} ET$

$$KE = \frac{3}{2} RT \text{ per mole or } E_T = \frac{3}{2} RT$$

$PV = RT = \frac{2}{3} E_T$, where E_T = Translational kinetic energy for 1 mole of gas

$$KE = \frac{3}{2} \times \frac{R}{N_0} \times T; \text{ KE per molecule} = KE = \frac{3}{2} KT$$

$\Rightarrow KE \propto T$, i.e. kinetic energy is directly proportional to temperature.

Hence, the translational kinetic energy of an ideal (perfect) gas is directly proportional to the absolute temperature.

MASTERJEE CONCEPTS

Boltzmann constant (k) = Gas constant per molecule.

$$= \frac{R}{N_0} = \frac{8.314 \text{ JK}^{-1} \text{ mol}^{-1}}{6.02 \times 10^{23} \text{ molecules mol}^{-1}} = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$$

T P Varun (JEE 2012, AIR 64)

7.1 Maxwell-Boltzmann Distribution of Molecular Speeds

At a particular temperature, different molecules of a gas possess different speeds. Further, as a result of continuous collisions among the molecules and against the walls of the container, their speeds keep on changing. However, Maxwell and Boltzmann showed that as a result of collisions, though some molecules are speeded up, some others are slowed down and thus the fractions of molecules possessing particular speeds remain constant at constant temperature. If fractions of molecules possessing particular speeds are plotted against their corresponding speeds at a particular temperature, a curve as shown in Fig. 3.7 is obtained. This distribution of speeds is known as Maxwell-Boltzmann distribution. From this curve, the following are observed:

- Fractions of molecules with too low or too high speeds are very small.
- The peak of the curve corresponds to a speed possessed by the maximum fraction or the maximum number of molecules. This speed is known as the most probable speed and is represented by c^* .

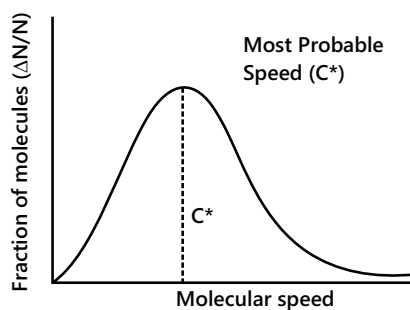


Figure 3.7: Maxwell-Boltzmann distribution curve

MASTERJEE CONCEPTS

- The peak (whole curve) shifts forward, which shows that the most probable velocity increases.
- The peak (whole curve) shifts downwards, which shows that the fraction of molecules or number of molecules possessing most probable velocity decreases.
- The curve is flattened (becomes broader) in the middle, which shows that more molecules have speeds near to the most probable speed.
- The fraction of molecules with higher speeds increases.
- The fraction of molecules with lower speed decreases.

It is, however, important to note that the total area under each of the curves remains the same as the sum of the fractions of molecules remains the same at any temperature.

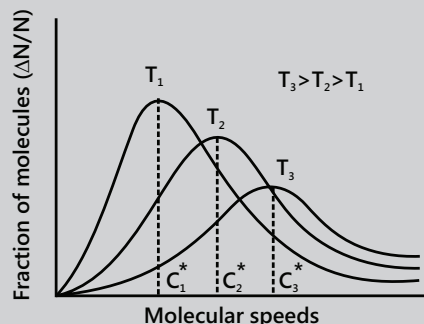


Figure 3.8: Maxwell-Boltzmann distribution curve at three different temperatures

B Rajiv Reddy (JEE 2012, AIR 11)

7.2 Kinds of Molecular Speeds

Molecular speeds are of three types, which are as follows:

1. Root mean square speed;
2. Average speed
3. Most probable speed

(a) Root mean square speed: The total kinetic energy of n molecules of a gas is the sum of the kinetic energy of the individual molecules.

$$\text{Total KE} = \frac{1}{2}mc_1^2 + \frac{1}{2}mc_2^2 + \frac{1}{2}mc_3^2 + \dots + \frac{1}{2}mc_n^2$$

Let c be the velocity possessed by each of the molecules

$$\Rightarrow \text{Total KE} = n \frac{1}{2}mc^2 \Rightarrow \frac{1}{2} \times n \times mc^2 = \frac{1}{2}mc_1^2 + \frac{1}{2}mc_2^2 + \frac{1}{2}mc_3^2 + \dots$$

$$\Rightarrow n \times c^2 = c_1^2 + c_2^2 + c_3^2 + \dots$$

$$c_{\text{rms}}^2 = \frac{c_1^2 + c_2^2 + c_3^2 + \dots}{n}; \quad c_{\text{rms}} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + \dots}{n}}$$

A much precise representation is $c_{\text{rms}} = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \dots}{n}}$; $n_T = n_1 + n_2 + n_3$

(b) Average Speed: It is defined as the arithmetic mean of various speeds of the molecules.

$$\text{Average speed} = \frac{c_1 + c_2 + c_3 + c_4 + \dots}{n} = \sqrt{\frac{8RT}{\pi M}} = 0.9213 \times c_{\text{rms}} \Rightarrow \text{RMS} = 1.085 \times c_{\text{av}}$$

3. Most probable speed: The speed possessed by the maximum number of molecules of a gas at a given temperature is called the most probable speed.

$$C_{mps} = \sqrt{\frac{2RT}{M}} = \left(\sqrt{\frac{2}{3}}\right) \times rms = 0.816 \times C_{rms}; C_{rms} = 1.224 \times C_{mps}$$

$$\text{Thus, } C_{mps} : C_{av} : C_{rms} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3} = 1 : 1.128 : 1.224$$

$$\text{Further, since } KE = \frac{1}{2} Mc^2 \Rightarrow KE \propto c^2 \text{ and } KE \propto T \Rightarrow c^2 \propto T \text{ or } c \propto \sqrt{T}$$

Hence, the molecular velocity of any gas is proportional to the square root of the absolute temperature. Therefore, the molecular motion is a thermal motion of the molecules. At absolute zero (i.e. $T = 0$), it is found that $KE = 0$. In other words, the thermal motion ceases completely at absolute zero.

MASTERJEE CONCEPTS

While calculating u , one should keep in mind the following:

(a) The proper units of terms

| | CGS | MKS |
|-----|----------------------|-------------------|
| u | cm/sec | m/sec |
| P | dyne/cm ² | N/m ² |
| V | cm ² | m ² |
| M | g | kg |
| R | erg | J |
| d | g/cm ³ | kg/m ³ |

A heavier gas has lower root mean square speed and diffuses slowly $\left(u_{rms} \propto \sqrt{\frac{1}{M}}\right)$

Curiosity Question: Molecular speeds of gaseous molecules are analogous to those of rifle bullets. Why is this odor of a gas not detected so fast?

Sol: Although the molecules of a gas travel at high speeds, they do not travel in straight lines in one direction like bullets. As they travel, they collide with the molecules of the gases that are present in the air. As a result, they become deflected. Hence, they follow a zigzag path, i.e. the net distance travelled in a particular direction is quite small in a given time. Hence, the odor is not detected so fast.

Aishwarya Karnawat (JEE 2012, AIR 839)

7.3 Equipartition of Energy

The total energy of a molecule is divided equally among the various degrees of freedom of a molecule. The distribution of kinetic energy along the axes x , y and z is $E_k = E_{kx} + E_{ky} + E_{kz}$.

As the motion of a molecule along the three Cartesian axes is equally probable, hence

$$E_{kx} = E_{ky} = E_{kz} = \frac{1}{3} \text{ of } E_k = \frac{1}{3} \left(\frac{3}{2} kT\right) = \frac{1}{2} kT, \text{ where } k = \text{Boltzmann constant} = \frac{R}{N_A}$$

This shows that each component of the kinetic motion contributes equally to the total kinetic energy and that the kinetic energy for each degree of freedom is $\frac{1}{2}kT$ per molecule or $\frac{1}{2}RT$ per mole.

With respect to vibrational motions, two atoms oscillate against each other. Therefore, the molecule possesses both potential energy and kinetic energy, which means that the energy of vibration involves two degree of freedom. Thus, the vibrational motion in a molecule is associated with energy

$$(a) \frac{1}{2}kT \text{ for potential energy} \quad (b) \frac{1}{2}kT \text{ for kinetic energy}$$

Thus, total vibration energy = Potential vibrational energy + Kinetic vibrational energy per molecule

$$= 2 \left(\frac{1}{2}kT \right) = 2 \left(\frac{1}{2}RT \right) \text{ per mole} \quad \left(\text{Since } k = \frac{R}{N_A} \Rightarrow R = kN_A \right)$$

MASTERJEE CONCEPTS

If a gaseous species has n_1 translation degree of freedom, n_2 rotational degrees of freedom and n_3 vibrational degrees of freedom, the total energy of species is given by:

$$n_1 \left(\frac{kT}{2} \right) + n_2 \left(\frac{kT}{2} \right) + n_3 \left\{ \left(\frac{kT}{2} \right) \times 2 \right\}$$

Saurabh Chaterjee (JEE Advanced 2013, AIR)

Illustration 13: Under 3 atm, 12.5 L of a certain gas has a weight of 15 g. What is the average speed of gaseous molecules?

$$\text{Sol: } u_{\text{avg}} = \sqrt{\frac{8RT}{\pi M}} \quad \dots (i)$$

$$\text{Given, } P = 3 \text{ atm, } V = 12.5 \text{ L, } w = 15 \text{ g}$$

Using the gas equation $PV = (w/m)RT$, we get

$$3 \times 12.5 = (15/m) \times 0.0821 \times T$$

$$\therefore T/m = 30.45 \quad \dots (ii)$$

From the equations (i) and (ii), we get $u_{\text{AV}} = 8.03 \times 10^4 \text{ cm sec}^{-1}$

Illustration 14: Find the temperature at which CO_2 has the same V_{rms} as that of O_2 ?

(JEE MAIN)

$$\text{Sol: For } \text{O}_2 = u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R \times 27}{32}}$$

$$\text{For } \text{CO}_2 = u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R \times T}{44}}$$

$$\text{As both are same, therefore, } \frac{3R \times 273}{32} = \frac{3RT}{44} \Rightarrow T = 375.38 \text{ K} = 102.38^\circ\text{C}$$

Illustration 15: (a) Calculate the total energy and average kinetic energy of 32 g of methane molecules at 27°C ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

(b) Calculate the root mean square speed, average speed and most probable speed of the methane molecules at 27°C .

(JEE ADVANCED)

Sol: (a) Total KE = $\frac{3}{2} nRT = \frac{3}{2} \times \frac{32}{16} \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$

Molar mass of $\text{CH}_4 = 16 \text{ g mol}^{-1} = 7482.6 \text{ J}$

Average KE, $\text{KE} = \frac{3}{2} KT = \frac{3}{2} \times \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{6.02 \times 10^{23} \text{ molecules mol}^{-1}} \times 300 \text{ K} = 6.21 \times 10^{-21} \text{ J molecule}^{-1}$

or = $\frac{3}{2} RT \text{ mol}^{-1} = \frac{3}{2} \times 0.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} = 374.13 \text{ J molecule}^{-1}$

(b) Root mean square speed, $c = \sqrt{\frac{3RT}{M}}$

Using CGS units, put $R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$, $T = 27 + 273 = 300 \text{ K}$

$M(\text{for } \text{CH}_4) = 16 \text{ g mol}^{-1}$, we get $u_{\text{r.m.s.}} = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{16}} = 6.839 \times 10^4 \text{ cm s}^{-1} = 683.9 \text{ ms}^{-1}$

Using SI units, put $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 300 \text{ K}$, $M = 16 \times 10^{-3} \text{ kg mol}^{-1}$, we get

$$c = \sqrt{\frac{3 \times 8.314 \times 300}{16 \times 10^{-3}}} = 683.9 \text{ ms}^{-1}$$

Similarly, calculate the average speed (\bar{c}) and most probable speed (c^*) by using the equations $\bar{c} = \sqrt{\frac{8RT}{\pi M}}$ and

$$c^* = \sqrt{\frac{2RT}{M}}$$

Or $\bar{c} = 0.921 \times c = 0.921 \times 683.9 \text{ m s}^{-1} = 629.9 \text{ m s}^{-1}$

And $c^* = 0.816 \times c = 0.816 \times 683.9 \text{ m s}^{-1} = 558.1 \text{ m s}^{-1}$

7.4 Collision Diameter

The kinetic theory of gases considers molecules as point masses. When two such molecules approach each other, a point is reached at which the mutual repulsion between the molecules becomes so strong that it causes reversal of the direction of their motions. The distance between the centers of the two molecules at the point of their closest approach is called collision diameter.

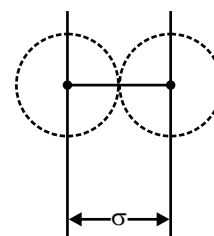


Figure 3.9: Collision diameter

7.5 Collision Number

The number of collisions with which a single molecule collides per unit time is given by $\sqrt{2} \pi \sigma^2 C_{\text{av}} \rho$ where C_{av} = average velocity, ρ = number density, i.e. number of molecules per unit volume of a gas. Thus, $Z_1 = \sqrt{2} \pi \sigma^2 C_{\text{av}} \rho$.

The total number of molecules that collide per unit time per unit volume of the gas is given by the equation $\sqrt{2} \pi \sigma^2 C_{\text{av}} \rho^2$. As each collision involves two molecules, the number of collisions of like molecules occurring per unit time

per unit volume of the gas is given by the equation $Z_{11} = \frac{1}{\sqrt{2}} (\sqrt{2} \pi \sigma^2 C_{\text{av}} \rho^2) = \frac{1}{\sqrt{2}} (\pi \sigma^2 C_{\text{av}} \rho^2)$. This is also known as collision frequency. Also, the number of collision of the molecules of type 1 with those of type 2 would be called

$$Z_{12} = \frac{1}{\sqrt{2}} (\pi \sigma^2 C_{\text{av}} \rho_1 \rho_2). \text{ Moreover, } \rho = \frac{P}{KT} = \text{Number density } z_{11} = \frac{1}{\sqrt{2}} \pi \sigma^2 C_{\text{av}} \times \frac{P^2}{(KT)^2}.$$

The frequency of collision is $\propto P^2$ and the frequency of collision is $\propto T^{3/2}$.

It should be noted that z_1 is expressed in s^{-1} , whereas z_{11} is expressed in $s^{-1}m^{-3}$.

7.6 Mean Free Path

Mean free path is the mean distance travelled by a gas molecule between two successive collisions.

$$\lambda = \frac{\text{Average distance travelled per second}}{\text{Number of collision by a molecule per sec}}; \lambda = \frac{c_{av}}{z_1} = \frac{c_{av}}{\sqrt{2}\pi\sigma^2 c_{av} P / KT} = \frac{KT}{\sqrt{2}\pi\sigma^2 P}$$

$$\Rightarrow \lambda \propto \frac{1}{P} \text{ at constant temperature, } \lambda \propto T \text{ at constant pressure}$$

8. BEHAVIOR OF REAL GASES - DEVIATIONS FROM IDEAL GAS BEHAVIOR

An ideal gas is a hypothetical gas whose pressure, volume and temperature behaviors are completely described by the ideal gas equation. Moreover, an ideal gas does not liquefy, but the case is exactly opposite for a real gas, which can be analyzed by observing the deviation from an ideal gas.

8.1 Deviations From Ideal Gas Behavior

The deviations from the ideal gas behavior are expressed in terms of compressibility factor (Z), where $Z = \frac{PV}{nRT} = \frac{PV}{RT}$ (for 1 mole) = $\frac{V_M}{V_{M \text{ ideal}}}$, where V_M is the actual molar volume of gas

MASTERJEE CONCEPTS

(a) Variation of Z with P and T

The values of Z exhibit both negative deviation ($Z < 1$) and positive deviation ($Z > 1$).

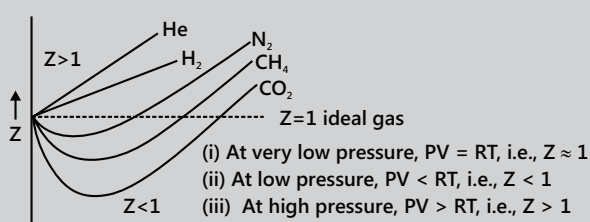


Figure 3.10 (a): Variation of compressibility factor against pressure

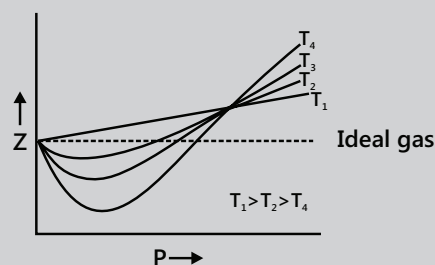


Figure 3.10 (b): Variation of compressibility factor against pressure

- (b) Exceptional behavior of H_2 and He: For these gases, experimental studies have revealed that $PV > RT$, i.e. $Z > 1$ or $V_M > 22.4 \text{ L}$ at NTP.
- (c) Deviation is more prominent at high P and low T .

Mredul Sharda (JEE Advanced 2013, AIR)

8.2 Real Gases

Van der Waals' Equation – A Modification in Gas Equation

Van der Waals pointed out that Maxwell had made two wrong assumptions in his kinetic theory of gases, which led to wrong results. According to van der Waals', it is not advisable to assume the following:

- (a) The volume occupied by the gaseous molecules is negligible as compared with the total volume of the gas at all conditions. Thus, van der Waals pointed out the two corrections in the gas equation.
- (b) The forces of attraction among gaseous molecules are negligible at all conditions.

Volume Correction

Excluded volume for one molecule in motion = $4v$

\therefore Excluded volume for 'N' molecules in motion = $4N.v$

\therefore Effective or excluded or co-volume of 1 mole = $4N.v = b$

Real or compressible or ideal volume of gas

= Actual volume of container – volume occupied by N molecules in motion

\therefore Real volume of a gas = $(V - b)$

Pressure Correction

Real pressure of a gas = Pressure developed due to collisions + Pressure loss due to attraction = $P + P'$

(Since in gases, a uniform distribution of molecules occurs)

Hence, $P' \propto n^2 \propto d^2 \propto \frac{1}{V^2}$, where d is the density of a gas and V is volume or $P' = \frac{a}{V^2}$, where a is van der Waals' constant of attraction.

The gas equation after the second correction is $\left[P + \left(\frac{a}{V^2} \right) \right] [V - b] = RT$.

8.3 Discussion of the van der Waals' Equation

- (a) **When pressure is not too high:** When pressure is not very high, volume V_m will be sufficiently large and b may be ignored in comparison. The van der Waals' equation for 1 mole of a gas

$$\left(P + \frac{a}{V_m^2} \right) (V_m - b) = RT \quad \dots \text{(i)}; \quad \left(P + \frac{a}{V_m^2} \right) V_m = RT$$

$$\text{or } PV_m + a/V_m = RT \text{ or } PV_m = RT - a/V_m \quad \dots \text{(ii)}$$

- (b) **When pressure is too high:** When pressure is considerably high, volume V_m will be quite small. It may not be possible to ignore b . As P is quite high, the quantity a/V_m^2 may become negligible in comparison with P in equation 6, which, therefore, reduced to

$$\begin{aligned} & P(V_m - b) = RT \\ \text{or} & \quad PV_m = RT + Pb \quad \dots \text{(iii)} \end{aligned}$$

- (c) **When temperature is high:** If, at a given pressure, temperature is considerably high, volume will become sufficiently large to make the value of a/V_m^2 negligibly small. At a high temperature, b may also be negligible in comparison to V_m , which is now sufficiently large. Under these conditions, the van der Waals' equation approaches the ideal gas equation, i.e. $PV_m = RT$, which explains why deviations become less at high temperatures.

- (d) **Exceptional behavior of hydrogen and helium:** As both hydrogen and helium have comparatively small masses, the attractive forces between their molecules are too small. In other words, the correction term a/V_m^2 due to the attraction factor is negligible at ordinary temperatures.

$$\text{Hence, } PV_m = RT + Pb. \quad \dots \text{ (iv)}$$

MASTERJEE CONCEPTS

The value of 'a' depends on the intermolecular forces (because it is a correction to it) and that of 'b' depends on the excluded volume.

The units of 'a' and 'b*' are as follows:

$$\text{Unit of 'a' (a = P} \times V^2) = \text{atm L}^2 \text{ mol}^{-2} \quad (\text{In L-atm})$$

$$= \text{dyne cm}^4 \text{ mol}^{-2} \quad (\text{In CGS})$$

$$= \text{N m}^4 \text{ mol}^{-2} \quad (\text{In MKS})$$

$$\text{or } = \text{kg m}^5 \text{ s}^{-2} \text{ mol}^{-2} \quad (\text{In MKS})$$

$$\text{Unit 'b' (b = 4Nv) L mol}^{-1} \quad (\text{In L-atm})$$

$$= \text{cm}^3 \text{ mol}^{-1} \quad (\text{In CGS})$$

$$= \text{m}^3 \text{ mol}^{-1} \quad (\text{In MKS})$$

Tendency of Liquefaction of a Gas

Easily liquefiable gases have greater intermolecular force, which is represented by a high value of 'a'. Hence, the greater the value of 'a,' more will be its liquefiability.

Easily liquefiable gases are: $\text{SO}_2 > \text{NH}_3 > \text{H}_2\text{O} > \text{CO}_2$, etc.

$\xrightarrow{\text{Decreasing value of constant 'a'}}$
(Decreasing tendency of liquefiability)

The above mentioned gases have a higher value of 'a' as compared with the permanent gases O_2 , N_2 , H_2 , He, Ne, etc.

If two gases have the same value for 'b' but different values for 'a', then the gas having a larger value of 'a' will occupy lesser volume because of more attraction among the molecules, thereby decreasing the distance between the molecules.

If two gases have the same values, for 'a' but different values for 'b', then the gas having a smaller value of 'b' will show more compressibility and will occupy lesser volume.

For a van der Waals' gas, if $a = 0$, then the compressibility factor versus pressure curve is linear with a positive slope, but not linear if $b = 0$.

For a van der Waals' gas, if neither $a = 0$ nor $b = 0$ shows minima and at the point of intersection $Z = 1$, a and b can be calculated.

Nikhil Khandelwal (JEE 2009, AIR 94)

9. CRITICAL PHENOMENON AND LIQUEFACTION OF GASES

The mathematical definition of the critical point is given by the following equation:

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

The critical isotherm on a p-V diagram has a point of inflection. Equations constitute a set of two equations in two unknowns, V and T. One can test to see whether an approximate equation of state gives a critical point by calculating these two derivatives for the equation of state and trying to solve the pair of equations. If a solution exists (T and V are neither zero nor infinity), then we say that the equation of state has a critical point.

Let us use this test to see whether a van der Waals' gas has a critical point. First, we need to solve the van der Waals' equation of state for pressure, p

$$P = \frac{nRT}{V - nb} - a \frac{n^2}{V^2} \quad \dots \text{(i)}$$

We can now take the derivatives and set them (independently) equal to zero.

$$\left(\frac{\partial p}{\partial V} \right)_T = -\frac{nRT}{(V - nb)^2} + 2a \frac{n^2}{V^3} = 0 \quad \dots \text{(ii)}$$

$$\left(\frac{\partial^2 p}{\partial V^2} \right)_T = \frac{2nRT}{(V - nb)^3} - 6a \frac{n^2}{V^4} = 0 \quad \dots \text{(iii)}$$

In order to stress that from here on the problem is pure algebra, let us now rewrite the simultaneous equations that must be solved for the two unknowns, V and T (which solutions we will call V_c and T_c)

$$-\frac{nRT}{(V - nb)^2} + 2a \frac{n^2}{V^3} = 0 \quad \dots \text{(iv)}$$

$$-\frac{2nRT}{(V - nb)^3} - 6a \frac{n^2}{V^4} = 0 \quad \dots \text{(v)}$$

There are many ways to solve simultaneous equations. One way is to multiply the equation (4) by $\frac{2}{V - nb}$

$$\text{to get } -\frac{2nRT}{(V - nb)^3} + 4a \frac{n^2}{V^3(V - nb)} = 0 \quad \dots \text{(vi)}$$

Now, add the equations (4) and (5). It should be noted that in this addition, the terms containing T will cancel out

$$\text{leaving } -\frac{6an^2}{V^4} + 4a \frac{n^2}{(V - nb)} = 0 \quad \dots \text{(vii)}$$

Divide the equation (7) by $2an^2$ and multiply it by V^3 (and bring the negative term to the other side of the equal

$$\text{sign) to get } \frac{2}{(V - nb)} = \frac{3}{V} \quad \dots \text{(viii),}$$

Which is easily solved to get the equation $V = V_c = 3nb$

To find the critical temperature, the critical volume should be substituted into one of the derivatives (which equals zero). This gives the following equation:

$$-\frac{nRT}{(3nb - nb)^2} + 2a \frac{n^2}{(3nb)^3} = 0 \quad \dots \text{(ix),}$$

$$\text{Which 'cleans up' to give the following equation: } = \frac{RT}{4} = \frac{2a}{27b} \quad \dots \text{(x)}$$

$$\text{or } T = T_c = \frac{8a}{27bR} \quad \dots \text{(xi)}$$

The critical pressure is obtained by the substitution of V_c and T_c into the van der Waals' equations of state.

$$P_c = \frac{nRT_c}{V_c - nb} - a \frac{n^2}{V_c^2} = \frac{nR \left(\frac{8a}{27bR} \right)}{3nb - nb} - a \frac{n^2}{(3nb)^2} \quad \dots \text{(xii)}$$

This simplifies to the following equation: $P_c = \frac{a}{27b^2}$... (xiii)

Our conclusion is that the van der Waals' equation of state gives a critical point since the set of simultaneous equations has a unique solution.

The van der Waals' equation of state is still an approximate equation of state and does not exactly represent any real gas. It has, however, some of the features of a real gas and is therefore useful as the next best approximation to a real gas. We will derive thermodynamic relationships (equations) using the ideal gas approximation. We can re-derive some of these equations using the van der Waals' equation of state to see how these relationships are affected by gas non-ideality. Hence, the conclusion is as follows:

Critical Temperature: It is defined as the temperature above which gases can never be liquefied; however, the pressure applied may be high.

$$T_c = \frac{8a}{27Rb}$$

Critical Pressure: The pressure just required to liquefy a gas at critical temperature is known as critical pressure.

$$P_c = \frac{a}{27b^2}$$

Critical Volume: The volume of a gas at the critical temperature and critical pressure is known as critical volume.
 $V_c = 3b$

MASTERJEE CONCEPTS

- For a gas having its temperature much lower than its critical temperature, less pressure is sufficient to liquefy it.

- The numerical value of $\frac{RT_c}{P_c V_c} = \frac{8}{3}$ (on substituting T_c, P_c, V_c)

Hence, one can write that the value of $\frac{RT}{PV}$ at critical conditions is $\frac{8}{3}$ of normal conditions.

$$\text{i.e. } \frac{RT_c}{P_c V_c} = \frac{8}{3} = \frac{8}{3} \times \frac{RT}{PV} \quad \left(\because \frac{RT}{PV} = 1 \right)$$

The values of $\frac{P_c V_c}{RT_c}$, i.e. Z at critical conditions can be written as equal to $\frac{3}{8}$ or 0.375

- Each gas has a characteristic temperature, which is known as inversion temperature (T_i) below which the gas on subjecting to JT effect shows cooling and above which it shows heating.

$$T_i = \left(\frac{2a}{Rb} \right)$$

Vaibhav Krishnan (JEE 2009, AIR 22)

9.1 Boyle Temperature

As already mentioned, the temperature at which a real gas obeys Boyle's law is called the Boyle temperature, T_B . It is represented by the expression $T_B = a/bR$

Hydrogen and helium show heating effect on adiabatic expansion (Joule-Thomson effect) since their inversion temperatures are low.

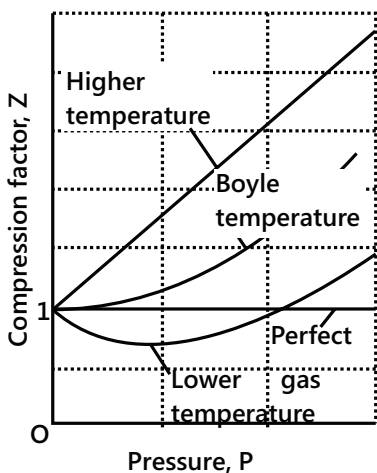


Figure 13 (a): The compression factor, Z , approaches 1 at low pressure, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas behaves perfectly over a wider range of conditions than at other temperatures

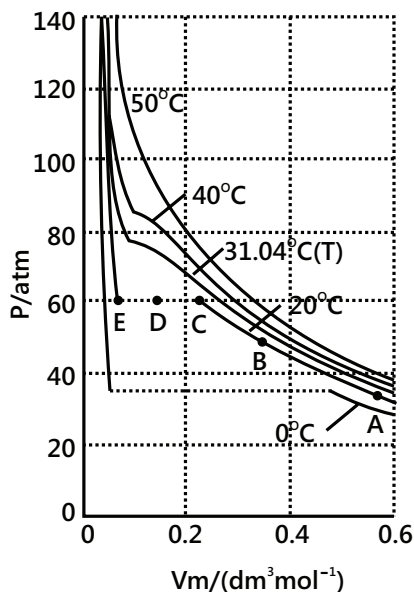


Figure 13 (b): Experimental isotherms of carbon dioxide at several temperatures. The critical isotherm, the isotherm at the critical temperature, is at 31.04°C . The critical point is marked with a star

Illustration 16: CO_2 has a compressibility factor of 0.2005 at 273 K and 100 atm pressure. What is the volume occupied by 0.2 mol of CO_2 gas at 100 atm and 273 K using (a) ideal gas nature and (b) real gas nature?

(JEE MAIN)

Sol: (a) For ideal gas, $Z = \frac{PV}{nRT}$ (for real gas, $Z = 1$)

$$1 = \frac{100 \times V}{0.2 \times 0.821 \times 273} \quad \therefore V = 0.0448 \text{ L}$$

(b) For real gas, $Z = \frac{PV}{nRT} \Rightarrow 0.2005 = \frac{100 \times V}{0.2 \times 0.821 \times 273}$

$$\therefore V = 8.98 \times 10^{-3} \text{ L}$$

Illustration 17: Using van der Waals' equation, find the value of the constant 'a' when two moles of a gas confined in a 4-L flask exerts a pressure of 11.0 atm at a temperature of 300 K. The value of 'b' is given as 0.05 L mol^{-1} .

(JEE MAIN)

Sol: (a) The van der Waals' equation for n moles of gas is $\left[P + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$

Given, $V = 4 \text{ L}$; $P = 11.0 \text{ atm}$, $T = 300 \text{ K}$, $b = 0.05 \text{ L mol}^{-1}$, $n = 2$

$$\text{Hence, } \left[11 + \frac{2^2 a}{4^2} \right] [4 - 2 \times 0.05] = 2 \times 0.0821 \times 300$$

$$\therefore a = 6.46 \text{ atm L}^2 \text{ mol}^{-2}$$

Illustration 18: One way of writing the equation of state for a real gas is $PV = RT \left[1 + \frac{B}{V} + \dots \right]$, where B is a constant. Now derive an approximate expression for b in terms of the van der Waals' constant 'a' and 'b'.

(JEE ADVANCED)

$$\text{Sol: } \left[P + \frac{a}{V^2} \right] [V - b] = RT \text{ or } P = \frac{RT}{(V - b)} - \frac{a}{V^2}$$

$$\text{Multiply by } [V], \text{ we get } PV = \frac{RTV}{V - b} - \frac{a \times V}{V^2} \text{ or } PV = RT \left[\frac{V}{(V - b)} - \frac{a}{VRT} \right]; \text{ or } PV = RT \left[\left(1 - \frac{b}{V} \right)^{-1} - \frac{a}{VRT} \right]$$

$$\text{Now, } \left[1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left[\frac{b}{V} \right]^2 + \left[\frac{b}{V} \right]^3 + \dots \therefore PV = RT \left[1 + \frac{b}{V} - \frac{a}{VRT} + \left(\frac{b}{V} \right)^2 \dots \right]$$

$$\text{or } PV = RT \left[1 + \left(b - \frac{a}{RT} \right) \cdot \frac{1}{V} + \left(\frac{b}{V} \right)^2 + \dots \right] \text{ Thus, } B = b - \frac{a}{RT}$$

Illustration 19: The vapor of a substance has a density of 0.36 kg m^{-3} at 1 atm pressure and 500 K temperature. Under the same conditions, the vapor effuses through a small hole at a rate of 1.33 times faster than oxygen.

(a) Find out (i) molecular weight, (ii) molar volume, (iii) compression factor (Z) of the vapor and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive.

(b) If the vapor behaves ideally at the temperature of 1000 K , then determine the average translational kinetic energy of a molecule.

$$\text{Sol: (a) (i) } \frac{r_{(v)}}{r_{(O_2)}} = \sqrt{\frac{M_{(O_2)}}{M_{(v)}}} = \therefore 1.33 = \sqrt{\frac{32}{M_{(v)}}} \quad \therefore M_{(v)} = 18.1$$

$$\text{(ii) Molar volume } (\bar{V}) = \frac{\text{Molar weight}}{\text{Density of 1 mole}} = \frac{18.1 \times 10^{-3}}{0.36} = 50.25 \times 10^{-3} \text{ m}^3$$

$$\text{(iii) Compression factor } (Z) = \frac{P\bar{V}}{RT} = \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500} \quad (P = 101325 \text{ Nm}^{-2} = 1 \text{ atm}) = 1.225$$

(iv) Repulsive forces operate among molecules since $Z > 1$

$$\text{(b) Average KE} = (3/2)kT = (3/2) \times 1.38 \times 10^{-23} \times 1000 = 2.07 \times 10^{-20} \text{ J/molecule}$$

9.2 The Liquid State

(a) Surface Tension: Surface tension of a liquid is defined as the force acting at right angles to the surface along a length of one centimeter of the surface. Surface tension is represented by the Greek letter gamma, γ .

Owing to surface tension, molecules tend to leave the surface, i.e. the surface of the liquid tends to contract to the smallest possible area for a given volume of the liquid. Further, for a given volume of a liquid, a sphere has the minimum surface area, which explains why the drops of a liquid are spherical. Hence, it is apparent that

in order to increase its surface area, force must be exerted to overcome the surface tension. In other words, work has to be done to increase the surface area. Hence, the surface tension of a liquid is defined as the work (energy) required to expand the surface of a liquid by unit area. Mathematically, surface tension = work done / change in area. Therefore, surface tension of a liquid may also be defined as the force in dynes necessary to rupture its surface along a length of one centimeter. In SI units, surface tension is defined as the force in Newton required to rupture a length of 1 meter of the surface of a liquid. Hence, the units of surface tension are dyne per cm (or Newton per meter in SI system).

Variation with Temperature: The surface tension of a liquid decreases with an increase of temperature and becomes zero at its critical temperature (where the surface of separation between the liquid and its vapor disappears). The decrease in surface tension with an increase of temperature is due to the fact that with an increase of temperature, the kinetic energy of the molecule (and hence the speed of molecules) increases and hence the intermolecular force of attraction decreases.

- (b) **Viscosity of Gases:** Viscosity is defined as the internal resistance that one part of a fluid offers to the flow of another part of the fluid. Similar to liquids, gases also show viscous behavior. For gases, we generally assume planes

at a distance of mean free path. The coefficient of viscosity (η) is given by the expression $\eta = \frac{5}{16\sigma^2} \left(\frac{mkT}{\pi} \right)^{1/2}$,

where k is the Boltzmann constant equal to R/N , η and m are diameter and mass of the molecule, respectively. Reciprocal of η gives fluidity. The variation of σ with pressure and temperature gives the nature of the intermolecular forces in the gas. The unit of viscosity is poise ($\text{dyne cm}^{-2} \text{ s}$) in cgs and Pascal second (Pa s) or Newton second per square meter (N s m^{-2}) in SI units. Viscosity of gases, unlike for liquids, increases with an increasing temperature and is independent of pressure.

- (c) **Vapor Pressure:** The movement of molecules from the liquid phase into the gas phase (i.e. evaporation) goes on continuously. If the surface over the liquid is covered, the molecules in the vapor phase return after collision with the covered area and, thus, strike the liquid surface and stick there (Figure 14). Furthermore, as the number of the gas-phase molecules increases, the probability increases that a molecule in the gas phase will strike the liquid surface and stick there. This phenomenon is known as condensation. The rate of evaporation remains constant with time, whereas the rate of condensation increases with time. Eventually, the two attain equilibrium. The number of molecules returning to the liquid exactly equals the number of molecules escaping from it. The number of molecules in the gas phase then attains a steady value and the pressure of the vapors at this stage becomes constant and is usually referred as vapor pressure.

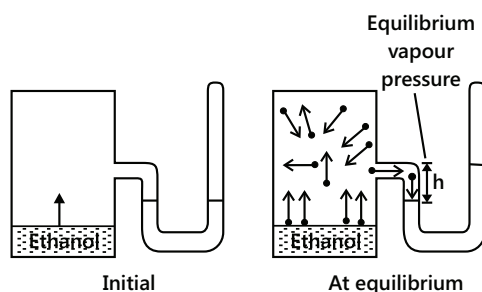


Figure 14: Vapour pressure of ethanol

- (i) **Nature of Liquids:** Liquids have different magnitudes of intermolecular attractive forces and, therefore, have different vapor pressures. Liquids with higher intermolecular attractive forces have lesser tendency for evaporation and thereby possess lower vapor pressure.
- (ii) **Temperature:** As the temperature of a liquid increases, the molecules move more energetically and can therefore escape more readily from their neighbors. Hence, vapor pressure of every liquid increases as the temperature increases.

$$2.303 \log \frac{P_2}{P_1} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right], \text{ where } \Delta H \text{ is heat of vaporization}$$

MASTERJEE CONCEPTS

Curiosity Question: Viscosity of a liquid is defined as its resistance to flow. Some liquids such as water and petrol flow very easily and are said to be less viscous. However, some liquids such as honey, syrup and ketchup flow with difficulty and are said to be highly viscous. The viscosity of liquids plays an important role in a number of items that we use in our day-to-day lives as well as in our health.

Answer the following questions:

- (i) By applying the concept of viscosity, explain the occurrence of cardiac arrest. Why there are a greater number of cardiac arrests in winter than in summer?
- (ii) What role does viscosity play in a hydraulic jack used to lift a heavy load such as car?
- (iii) What role does viscosity plays in automatic door closers?
- (iv) What role does viscosity plays in shock absorbers used in cars, scooters and motorbikes?
- (v) Glass is considered to be a highly viscous liquid. If it were not, then what would have happened?

Ans. (i) Blood is a viscous liquid that flows through blood vessels. It flows to the heart through arteries. When a person eats a diet rich in fats, these fats start getting deposited inside the arteries. As a result, the arteries become narrowed and the flow of blood through them becomes difficult. When the blockage in the arteries exceeds a particular limit, the flow of blood to the heart stops, resulting in a cardiac arrest. In winter, people normally overeat, especially ghee products. As a result, deposition of fats in the arteries increases. Moreover, in winter, people smoke and drink more because of the misconception that smoking and drinking give warmth to the body, In fact, smoking and drinking damage the organs and slowdown the flow of blood to the heart.

- (ii) A hydraulic jack depends on the viscosity of the oil to control the rate of fall when lowering the load, i.e. car.
- (iii) Automatic door closers are often filled with oil. These closers use the viscosity of the oil to control the speed of the door as it closes.
- (iv) A shock absorber uses the viscosity of its oil content to damp out the shock motion imparted by an uneven road surface.
- (v) If glass were not as viscous as it actually is, the lasting of windows would not have been long.

Mredul Sharda (JEE Advanced 2013, AIR)

PROBLEM-SOLVING TACTICS

(a) Molar volume at STP:

- (i) When STP conditions are taken as 0°C and 1 atm pressure, then the molar volume of a gas = 22,400 mL.
- (ii) When STP condition are taken as 0°C and 1 bar pressure, then the molar volume of a gas = 22,700 mL.
- (iii) When SATP conditions are used, i.e. 25°C (298.15 K) and 1 bar pressure, then the molar volume = 24,800 mL.

- (b) While solving a problem, the value of 'R' can be taken as 22.4/273. As a result, the calculation becomes easy when STP conditions are mentioned and the terms will easily cancel out. Moreover, note the values of 'R' to be used in different units.

The gas constant (R)

$$8.31447 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$8.20574 \times 10^{-2} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$$

$$8.31447 \times 10^{-2} \text{ m}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$$

$$8.31447 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$162.364 \text{ dm}^3 \text{ torr K}^{-1} \text{ mol}^{-1}$$

$$1.98721 \text{ cal K}^{-1} \text{ mol}^{-1}$$

- (c) Dalton's law is valid for gases that do not react chemically, e.g. the law is not valid for a mixture of SO_2 and O_2 . This is because of the fact that Dalton's law involves conservation of moles, whereas in chemical reaction conservation of moles is not noticed.

POINTS TO REMEMBER

