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.

$$\text{Ice} \rightleftharpoons \text{Water} \rightleftharpoons \text{Vapor}$$

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.

$$\text{Solid} \underset{\text{Cool(freezing)}}{\overset{\text{Heat(fusion)}}{\rightleftharpoons}} \text{Liquid} \underset{\text{Cool(condensation)}}{\overset{\text{Heat(evaporation)}}{\rightleftharpoons}} \text{Gas}\,;\ \text{Solid} \underset{\text{Hoar frosting}}{\overset{\text{Sublimation}}{\rightleftharpoons}} \text{Vapor}$$

1.2 The Gaseous State

Measurable Properties of Gases

(a) **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

(b) **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 expresses as $1\ m^3 = 10^3\ L = 10^3\ dm^3 = 10^6\ cm^3$

(c) **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 = ^{o}C + 273.15

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

0°C = 32°F and 37°C = 98.6°F (human body temperature)

(d) **Pressure:** The force experiended 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 mesaurd 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 atm = 76 cm = 760 mm or 760 torr

The unit of pressure commonly used is 'bar.'

1 atm = 1.01325 bar or 1 bar = 0.987 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 Pa = 1 Nm^{-2} = 1 kg m^{-1} 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 atm = 76.0 cm of mercury = 760 mm of mercury = 760 torr = 1.01325×10^5 Pa

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:

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

CONCEPTS

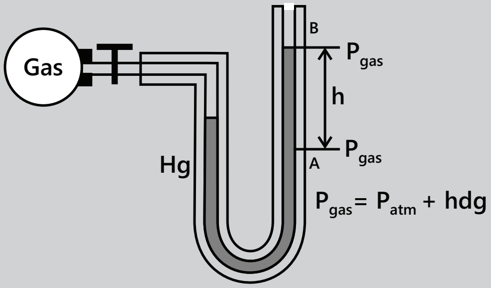


Figure 3.1: An open arm manometer

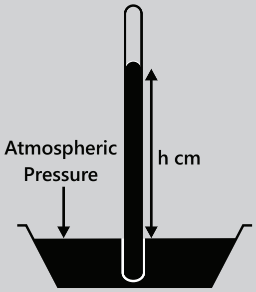


Figure 3.2: Barometer

Things to Remember:

Name	Symbol	Value
Pascal	1 Pa	1 Nm^{-2}, 1 kg $m^{-1}s^{-2}$
Bar	1 bar	10^5 Pa
Atmosphere	1 atm	101.325 kPa
Torr	1 torr	101 325/760 Pa = 133.32 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: 0ºC or 273.15 K temperature and 1 atm (=1.01325 bar) pressure

Standard Ambient Temperature and Pressure (SATP)

SATP conditions: 298.15 K (25°C) and 1 bar (105 Pa) pressure

The molar volume of an ideal gas at SATP conditions is 24.789 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.

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

Log P + log V = constant

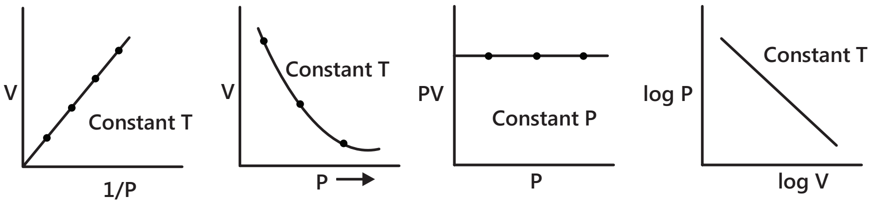


Figure 3.3: Various plots of pressure (P) vs Volume (V)

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) $\Rightarrow V = KT \Rightarrow \frac{V}{T}$ = constant = K

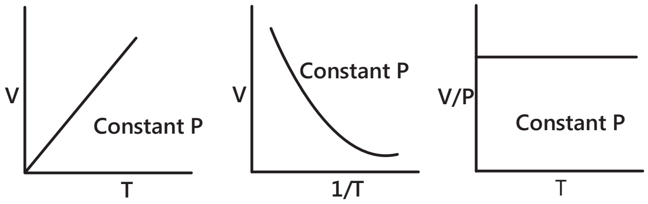


Figure 3.4: Various plot of volume (V) vs Temperature (T)

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).

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

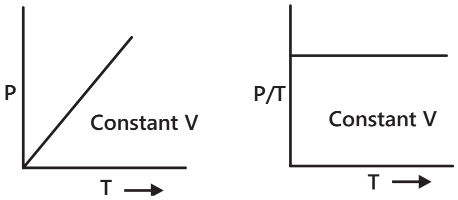


Figure 3.5: Plots of pressure (P) vs Temperature (T)

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)

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:

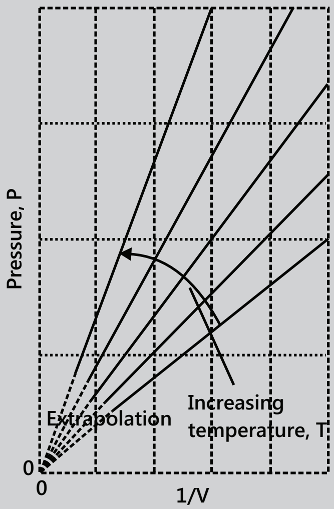


Figure 3.6 (a): Straight lines are obtained when the pressure is plotted against 1/V at constant temperature

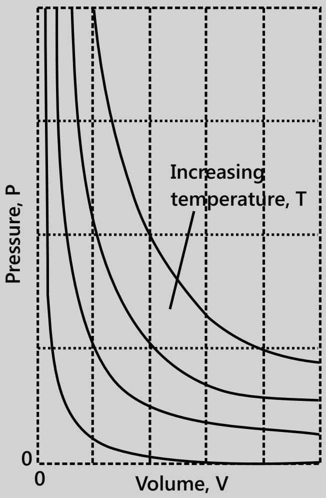


Figure 3.6 (b): The pressure-volume dependence of a fixed amount of perfect gas at different temperatures. Each cure is a hyperbola (pV = constant) and is called an isotherm

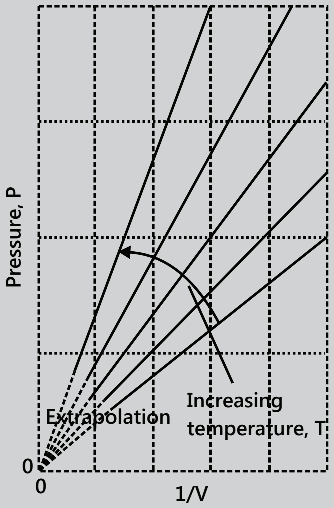


Figure 3.6 (c): The pressure also varies linearly with the temperature at constant volume and extrapolates to zero at T = 0 (-273°C)

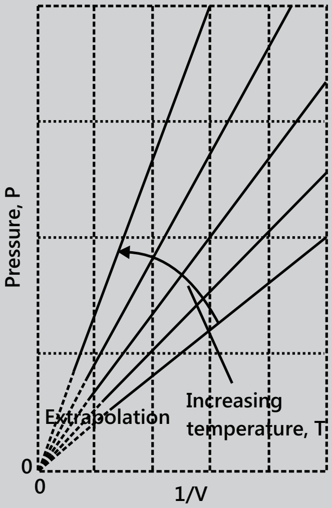


Figure 3.6 (d): The variation of the volume of a fixed amount of gas with the temperature at constant pressure. Note that in each case the isobars extrapolate to zero volume at T = 0 or θ = -273°C

CONCEPTS

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: $\frac{PV}{T}$ = Constant $\Rightarrow \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- 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 atm; V = 22.4 L; T = 273 K; n = 1 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 = Number of moles = $\frac{\text{amount of gas}}{\text{Mol. wt of gas}} = \frac{w}{M_0}$

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

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

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

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)

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

Let 'n' balloons are filled, then the total volume of H_2 used in filling the balloons = 4.851 x 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

$= 4.851 \text{ x } n + 2.82$ ... (i)

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

P = 1 atm, V = ? T = 273 K And P = 20 atm, V = 2.82 L, T = 300 K

$$\therefore \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \text{ or } \frac{1 \times V}{273} = \frac{20 \times 2.82}{300} = 51.32$$

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

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, $\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow \frac{3}{290} = \frac{P}{320} \Rightarrow P\ \ 3.31$ 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 atm 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 $P_1V_1 = P_2V_2$

$0.31 \times 10 = 1 \times V \Rightarrow V = 3.1$ 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 K

$\because PV = nRT$

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

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

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

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 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.

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

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.

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

Where PA, PB, 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:

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

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

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°C and p is the aqueous tension at that temperature, then according to Dalton’s law of partial pressures

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

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, $P_{moist} = P_{dry\ gas} + P_{H_2O}$ vapor (Since $P_{moist\ gas} > P_{Dry\ gas}$)

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

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

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 = 100 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 mL	V_2 = 1000 mL
P_1 = 760 mm	P_2 = ? (Dry state)
T_1 = 273 K,	T_2 = 273 + 15 = 288 K

By applying gas equation, we get

$$\frac{760\times919}{273} = \frac{P_2\times1000}{288} \text{ or } P_2 = \frac{760\times919\times288}{1000\times273}\text{ mm}$$

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 $\frac{P_1V_1}{T_2} = \frac{P_2V_2}{T_2}$, we get $\frac{760\times919}{273} = \frac{(750-p)\times1000}{288}$

Solve for p.

Illustration 7: The density of a mixture of O_2 and N_2 at NTP is given as 1.3g/L. Calculate the partial pressure of O_2. **(JEE ADVANCED)**

Sol: Let n_1 and n_2 be the moles of O_2 and N_2, respectively, in the mixture

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

For mixture: PV = (w/m)RT or $m = \frac{w}{VP}$. $RT = \frac{1.3\times0.0821\times273}{1}$ ... (ii)

m = 29.137

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

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

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

or $\frac{4n_1}{n_1+n_2} = 29.137 - 28$ or $\frac{n_1}{n_1+n_2} = 0.28$, i.e. mole fraction of O_2 = 0.28

Now, P'_{O_2} = PM × mole fraction of O_2 = 1 × 0.28 = 0.28 atm

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

$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g) \longrightarrow N_2O_4\ (s)$$

The dimer N_2O_4 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 O_2 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 mL, T = 300 K, P = 1.053 atm

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

For O_2: V = 100 mL, T = 300 K, P = 0.789

$$\therefore n_{O_2} = \frac{PV}{RT} = \frac{0.789\times 100}{0.0821\times 300\times 1000} = 0.32\times 10^{-2}$$

For the reaction	$2NO(g)$	+	$O_2(g)$	$\rightarrow$	$N_2O_4(s)$
Moles before the reaction	1.069×10^{-2}		0.32×10^{-2}		0
Moles of NO after the reaction	$(1.069\times 10^{-2} - 0.32\times 10^{-2}\times 2)$ $= 0.429\times 10^{-2}$		0		0.32×10^{-2}

$\therefore$ The gas left is NO, which is

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

Moreover, P × V = nRT

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

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

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

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

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

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

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

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

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

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

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

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

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

or $\frac{w_1}{t_1}\times\frac{t_2}{w_2}=\sqrt{\frac{M_1}{M_2}}$ ... (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. $-\frac{dP}{dt}$

$$\therefore\ -\frac{dP}{dt}\propto\frac{P}{\sqrt{M}}=\frac{KP}{\sqrt{M}} \text{ or } P_2 = P_1e^{\frac{Kt}{\sqrt{M}}}$$

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

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

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

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

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

Now, PV = nRT

$\therefore\ P\times 33.6=\frac{3}{2}\times 0.0821\times 546$ $\therefore\ P = 2$ 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.

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

Now, for diffusion of the gaseous mixture and pure O_2

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

$$\therefore M_m = 34.92 \qquad .... \text{(ii)}$$

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 N_2 and the other with 1 kg of H_2. The N_2 balloon leaks to a pressure of 1/2 atm in 1 h. How long would it take for the H_2 balloon to reach a pressure of 1/2 atm? **(JEE ADVANCED)**

Sol: Given for N_2: initially, $P_1 = 2$ atm $w_1 = 14$ kg (diffusion time 1 h)

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

Since for a gas at constant V and T, $P \propto w$

$$\therefore \frac{P_1}{P_2} = \frac{w_1}{w_2} \text{ or } \frac{2}{1/2} = \frac{14}{w_2} \quad \therefore w_2 = \frac{14}{4} \text{ kg } N_2$$

$\therefore$ The weight of N_2 diffused in 1 h = 14 − (14/4) = (21/2) kg

Similarly for H_2: initially $P_1 = 2$ atm, $w_1 = 1$ kg (diffusion time t h)

After diffusion, $P_2 = \frac{1}{2}$ 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 N_2 and H_2, t_{H_2} = 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 min

Illustration 12: A mixture containing 2.24 L of H_2 and 1.12 L of D_2 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 D_2. Calculate the % by weight of the gases in the second bulb. **(JEE ADVANCED)**

Sol: In bulb I before diffusion:

At STP, H_2 = 2.24 L = 0.2 g = 0.1 mole; D_2 = 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, $P \propto n$

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

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

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

$\therefore$ 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

$$\frac{1}{2}MV_A^2 + \frac{1}{2}MV_B^2 = \frac{1}{2}MV'^2_A + \frac{1}{2}MV'^2_B \Rightarrow V_A^2 + V_B^2 = V'^2_A + V'^2_B$$

(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, $n = 6.023 \times 10^{23} = Na$

$\Rightarrow n \times m = m \times Na = 6.023 \times 10^{23} \times m = M \Rightarrow PV = \frac{1}{3} Mc^2$ 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

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

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

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

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

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

KE = $\frac{3}{2} \times \frac{R}{N_0} \times T$; 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.

CONCEPTS

Boltzmann constant (k) = Gas constant per molecule.

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

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:

(i) Fractions of molecules with too low or too high speeds are very small.

(ii) 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*.

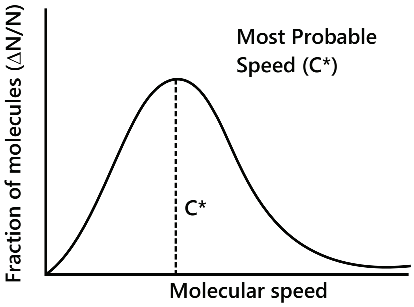


Figure 3.7: Maxwell-Boltzmann distribution curve

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.

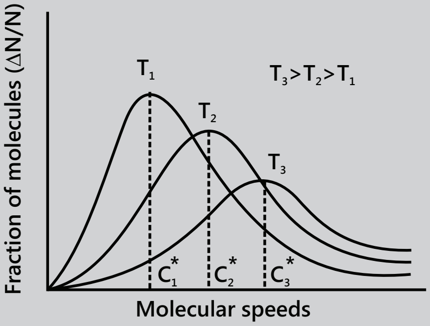


Figure 3.8: Maxwell-Boltzmann distribution curve at three different temperatures

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.

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

Let c be the velocity possessed by each of the molecules

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

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

$$c_{rms}^2 = \frac{c_1^2 + c_2^2 + c_3^2 + ...}{n}; \qquad c_{rms} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 + ...}{n}}$$

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

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

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

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.

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

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

Further, since $KE = \frac{1}{2} Mc^2 \quad \Rightarrow KE \propto c^2$ and $KE \propto T \quad \Rightarrow c^2 \propto T$ 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.

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

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

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

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?

Sol: $u_{avg} = \sqrt{[(8RT)/\pi M]}$ ... (i)

Given, P = 3 atm, V = 12.5 L, w = 15 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 ... (ii)

From the equations (i) and (ii), we get uAV = 8.03×10^4 cm sec^{-1}

Illustration 14: Find the temperature at which CO_2 has the same Vrms as that of O_2? **(JEE MAIN)**

Sol: For $O_2 = u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R\times 27}{32}}$

For $CO_2 = u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3R\times T}{44}}$

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

Illustration 15: (a) Calculate the total energy and average kinetic energy of 32 g of methane molecules at 27°C (R = 8.314 J K^{-1} 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 = $\frac{3}{2} \times \frac{32}{16}$ mol × 8.314 J K^{-1} mol^{-1} × 300 K

Molar mass of CH_4 = 16 g mol^{-1} = 7482.6 J

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

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

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

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

M(for CH_4) = 16 g mol^{-1}, we get $u_{r.m.s.}$ = $\sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{16}}$ = 6.839 × 10^4 cm s^{-1} = 683.9 ms^{-1}

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

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

Similarly, calculate the average speed ($\vec{c}$) and most probable speed (c*) by using the equations $\vec{c} = \sqrt{\frac{8RT}{\pi M}}$ and $c^* = \sqrt{\frac{2RT}{M}}$.

Or $\vec{c}$ = 0.921 × c = 0.921 × 683.9 m s^{-1} = 629.9 m s^{-1}

And c* = 0.816 × c = 0.816 × 683.9 m s^{-1} = 558.1 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 collisions diameter.

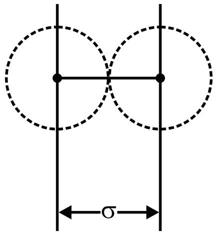


Figure 3.9: Collision diameter

7.5 Collision Number

The number of collisions with which a single molecule collides per unit time is given by $\sqrt{2}\ \overline{\pi}\sigma^2\ C_{av}\rho$ where c_{av} = average velocity, ρ = number density, i.e. number of molecules per unit volume of a gas. Thus, $Z_1 = \sqrt{2}\ \pi\sigma^2 C_{av}\rho$. The total number of molecules that collide per unit time per unit volume of the gas is given by the equation $\sqrt{2}\ \pi\sigma^2 C_{av}\rho^2$. 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 $Z_{11} = \frac{1}{\sqrt{2}} (\sqrt{2}\pi\sigma^2 C_{av}\rho^2) = \frac{1}{\sqrt{2}} (\pi\sigma^2 C_{av}\rho^2)$. 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 $z_{12} = \frac{1}{\sqrt{2}} (\pi\sigma^2 C_{av}\ \rho_1\rho_2)$. Moreover, $\rho = \frac{P}{KT}$ = Number density $z_{11} = \frac{1}{\sqrt{2}}\ \pi\sigma^2 c_{av} \times \frac{P^2}{(KT)^2}$.

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

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.

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

$\Rightarrow \lambda \propto \frac{1}{P}$ at constant temperature, $\lambda \propto T$ 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 VM is the actual molar volume of gas

CONCEPTS

(a) Variation of Z with P and T

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

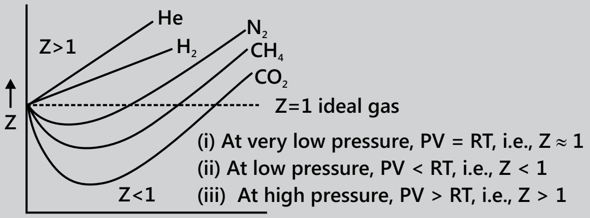


Figure 3.10 (a): Variation of compressibility factor against pressure

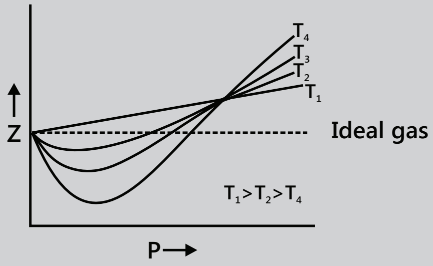


Figure 3.10 (b): Variation of compressibility factor against pressure

(b) Exceptional behavior of H_2 and He: For these gases, experimental studies have revealed that PV > RT, i.e. Z > 1 or VM > 22.4 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

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

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

(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

$$P(V_m - b) = RT$$

$$\text{or} \quad PV_m = RT + Pb \quad \text{... (iii)}$$

(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.

Hence, $PV_m = RT + Pb$. ... (iv)

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:

Unit of 'a' ($a = P \times V^2$) = atm L^2 mol^{-2} (In L-atm)
= dyne cm^4 mol^{-2} (In CGS)
= N m^4 mol^{-2} (In MKS)
or = kg m^5 s^{-2} mol^{-2} (In MKS)
Unit 'b' ($b = 4Nv$) L mol^{-1} (In L-atm)
= cm^3 mol^{-1} (In CGS)
= m^3 mol^{-1} (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: $\xrightarrow[\substack{\text{Decreasing value of constant'a'} \\ \text{(Decreasing tendency of liquefiability)}}]{SO_2 > NH_3 > H_2O > CO_2 \text{.etc}}$

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:

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

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

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

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

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

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

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)

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

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

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

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

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

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

sign) to get $\frac{2}{(V - nb)} = \frac{3}{V}$ ... (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:

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

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

or $T = T_C = \frac{8a}{27bR}$ ... (xi)

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

$$P_c = \frac{nRT_C}{V_C - nb} - a\frac{n^2}{V_C^2} \qquad = \frac{nR\left(\frac{8a}{27bR}\right)}{3nb - nb} - a\frac{n^2}{(3nb)^2} \qquad \text{... (xii)}$$

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 Walls' 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. $V_c = 3b$

CONCEPTS

- For a gas having its temperature much lower than its critical temperature, less pressure is sufficient to liquefy it.
- The numerical value of $\frac{RT_C}{P_CV_C} = \frac{8}{3} =$ (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.

  i.e. $\frac{RT_C}{P_CV_C} = \frac{8}{3} = \frac{8}{3} \times \frac{RT}{PV}$ $\left(\because \frac{RT}{PV} = 1\right)$

  The values of $\frac{P_CV_C}{RT_C}$, 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, TB. 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.

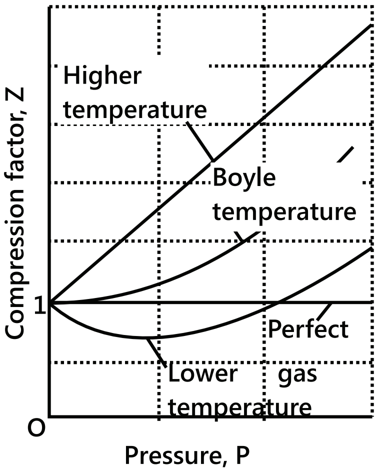


Figure 13 (a): The compression factor, Z, approaches 1 at low pressure, but does so with different slopes. For a perfect gas, the slope is zero, but real gases may have either positive or negative slopes, and the slope may vary with temperature. At the Boyle temperature, the slope is zero and the gas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

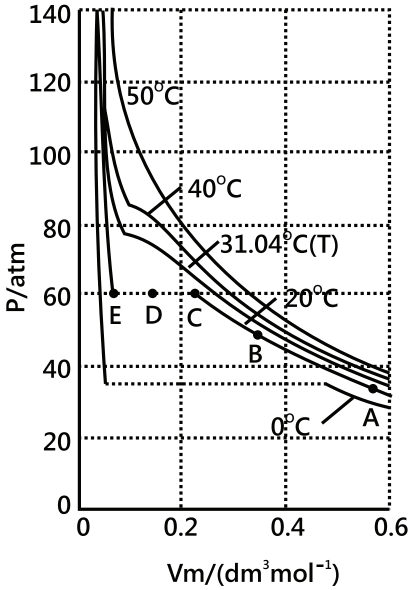


Figure 13 (b): Experimental isotherms of carbon dioxide at several temperatures. The critical isotherm, the isotherm at the critical temperature, is at 31.04°C. The critical point is markerd with a star

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)

$I = \frac{100 \times V}{0.2 \times 0.821 \times 273}$ $\therefore$ V = 0.0448 L

(b) For real gas, $Z = \frac{PV}{nRT} \Rightarrow 0.2005 = \frac{100 \times V}{0.2 \times 0.0821 \times 273}$

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

Illustration17: 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 $\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$

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

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

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

Illustration 18: One way of writing the equation of state for a real gas is PV = RT $\left[1+\frac{B}{V}+\ldots\ldots\right]$, 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)

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

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

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

or PV = RT $\left[1+\left(b-\frac{a}{RT}\right).\frac{1}{V}+\left(\frac{b}{V}\right)^2+\ldots\ldots\right]$ 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.

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

(ii) Molar volume ($\overline{V}$) = $\frac{\text{Molar weight}}{\text{Density of 1 mole}}=\frac{18.1\times10^{-3}}{0.36}$ = 50.25 × 10^{-3} m^3

(iii) Compression factor (Z) = $\frac{P\overline{V}}{RT}=\frac{101325\times50.25\times10^{-3}}{8.314\times500}$ (P = 101325 Nm^{-2} = 1 atm) = 1.225

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

(b) Average KE = (3/2)kT = (3/2) × 1.38 × 10^{-23} × 1000 = 2.07 × 10^{-20} 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 (dyne cm^{-2} 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.

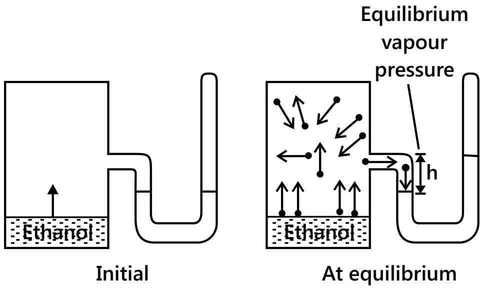


Figure 14: Vapour pressure of ethanol

(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.

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

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 J K^{-1} mol^{-1}

8.20574 × 10^{-2} m^3 atm K^{-1} mol^{-1}

8.31447 × 10^{-2} m^3 bar K^{-1} mol^{-1}

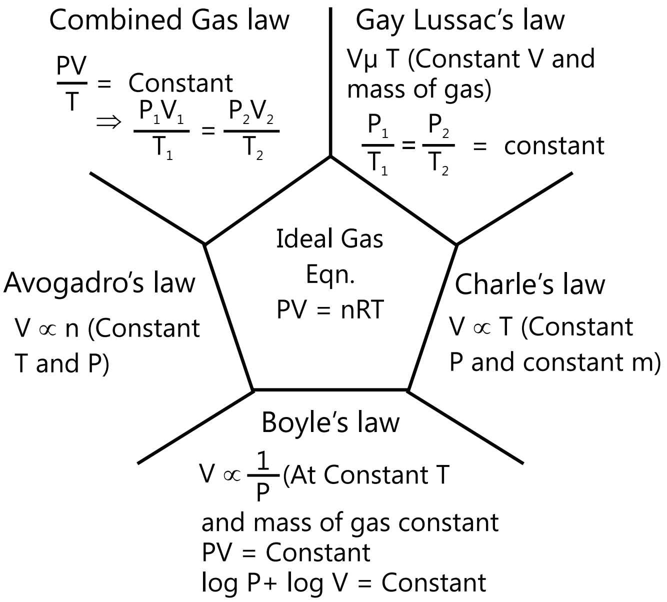
8.31447 Pa m^3 K^{-1} mol^{-1}

162.364 dm^3 torr K^{-1} mol^{-1}

1.98721 cal K^{-1} 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



Combined Gas law

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

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

Gay Lussac's law

Vμ T (Constant V and mass of gas)

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

Ideal Gas Eqn.

PV = nRT

Avogadro's law

V ∝ n (Constant T and P)

Charle's law

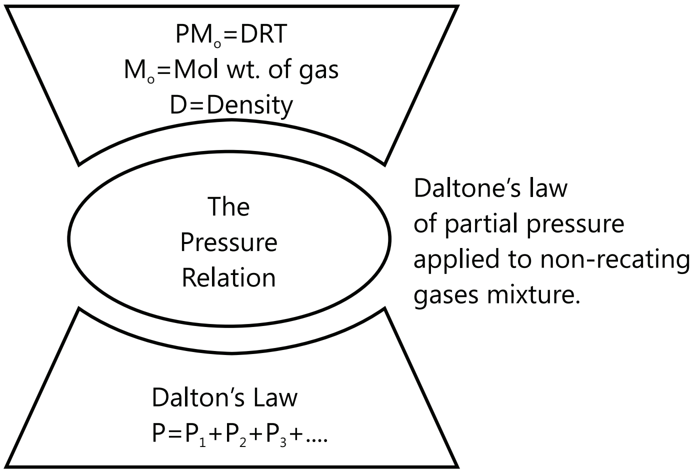
V ∝ T (Constant P and constant m)

Boyle's law

$V \propto \frac{1}{P}$ (At Constant T and mass of gas constant

PV = Constant

log P+ log V = Constant



PM_o=DRT

M_o=Mol wt. of gas

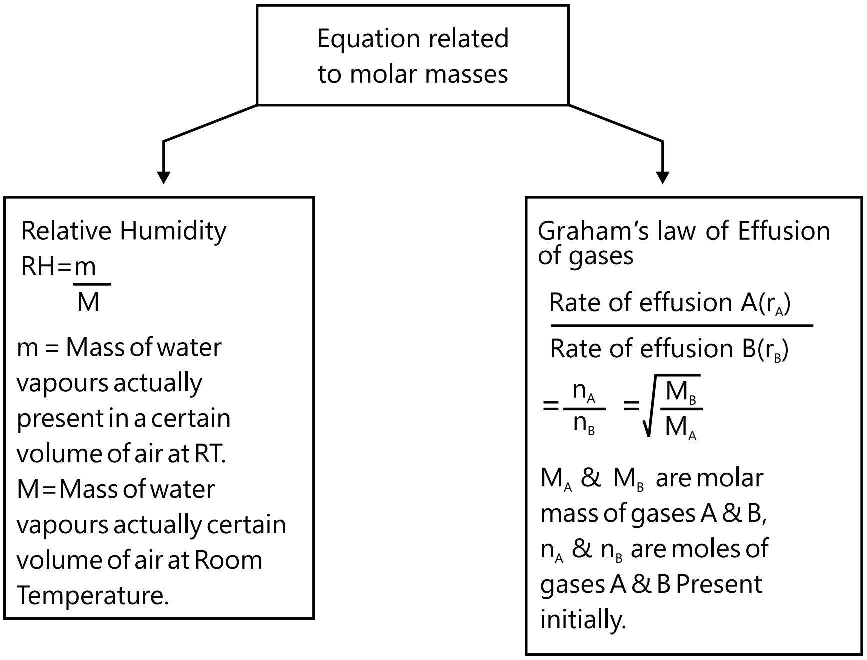
D=Density

The Pressure Relation

Daltone's law of partial pressure applied to non-recating gases mixture.

Dalton's Law

$P=P_1+P_2+P_3+....$



Equation related to molar masses

Relative Humidity

$RH = \frac{m}{M}$

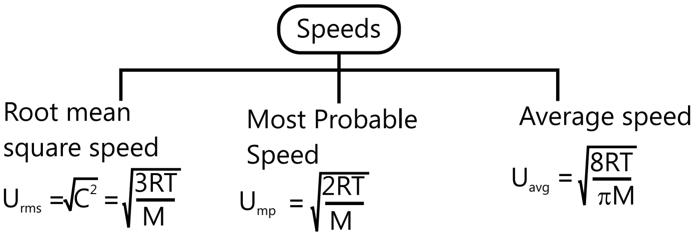
m = Mass of water vapours actually present in a certain volume of air at RT.

M = Mass of water vapours actually certain volume of air at Room Temperature.

Graham's law of Effusion of gases

$$\frac{\text{Rate of effusion A}(r_A)}{\text{Rate of effusion B}(r_B)} = \frac{n_A}{n_B} = \sqrt{\frac{M_B}{M_A}}$$

M_A & M_B are molar mass of gases A & B, n_A & n_B are moles of gases A & B Present initially.



Speeds

Root mean square speed

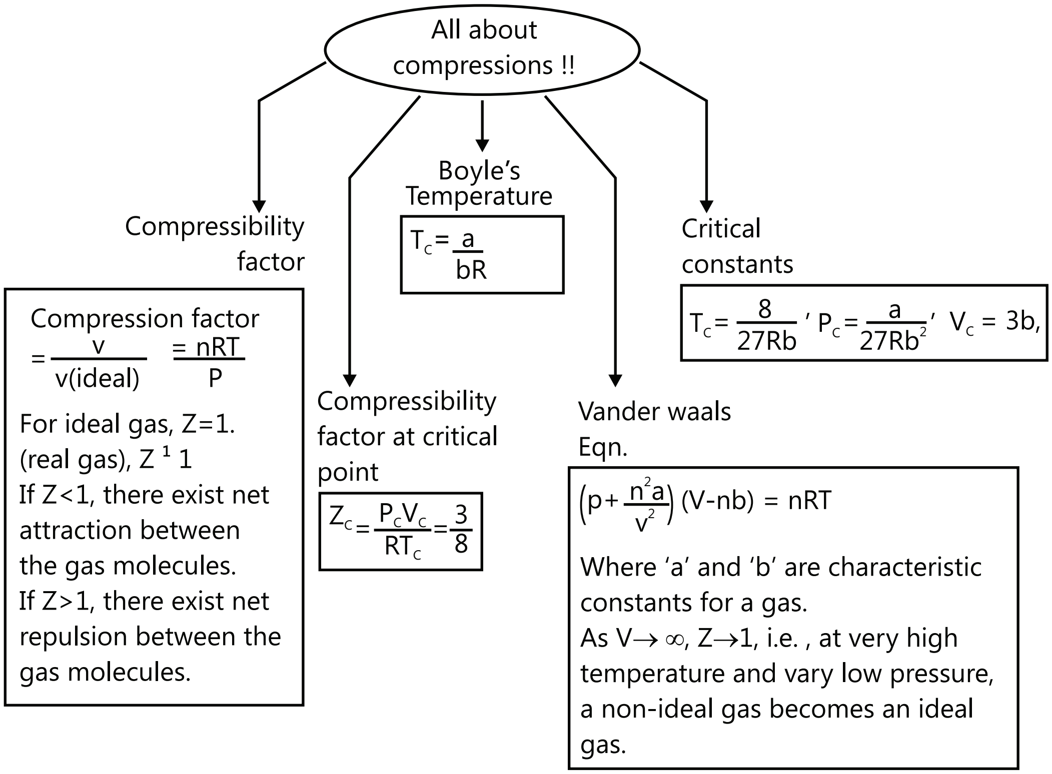
$U_{rms} = \sqrt{C^2} = \sqrt{\frac{3RT}{M}}$

Most Probable Speed

$U_{mp} = \sqrt{\frac{2RT}{M}}$

Average speed

$U_{avg} = \sqrt{\frac{8RT}{\pi M}}$



All about compressions !!

Compressibility factor

Compression factor $= \frac{v}{v(\text{ideal})} = \frac{nRT}{P}$

For ideal gas, Z=1.

(real gas), $Z\,^{1}\,1$

If Z<1, there exist net attraction between the gas molecules.

If Z>1, there exist net repulsion between the gas molecules.

Compressibility factor at critical point

$Z_C = \frac{P_C V_C}{RT_C} = \frac{3}{8}$

Boyle's Temperature

$T_C = \frac{a}{bR}$

Vander waals Eqn.

$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

Where 'a' and 'b' are characteristic constants for a gas.

As V→ ∞, Z→1, i.e. , at very high temperature and vary low pressure, a non-ideal gas becomes an ideal gas.

Critical constants

$T_C = \frac{8}{27Rb}$ ' $P_C = \frac{a}{27Rb^2}$' $V_C = 3b$,

Solved Examples

JEE Main/Boards

Example 1: At 27°C, volume of 95 mL of N_2O is collected in a graduated tube over mercury, the level of mercury inside the tube being 60 mm above the outside mercury level when barometer reads 750 mm.

(a) What is the volume of the same mass at STP?

(b) What volume would the same mass of a gas occupy at 40°C when the barometer pressure is 745 mm and the level of mercury inside the tube is 25 mm below the outside level?

Sol: Use the combined gas law equation.

(a) Given, T = 300 K

At STP,

V = (95/1000) mL; V =?

P = (750 – 60) mm = 690 mm, P = 1 atm

= (690/760) atm, T = 273 K

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

$$\frac{690 \times 95}{760 \times 300 \times 1000} = \frac{1 \times V}{273}$$

V = 0.07848 L = 78.48 mL

(b) At T = (40 + 273) K = 313 K [case (a) data]

P = (745+25) mm = 770 mm, T=300 K

$$= \frac{770}{760} \text{ atm} \qquad P = \frac{690}{760} \text{ atm}$$

$$V = ? \qquad V = \left(\frac{95}{1000}\right) L$$

$$\therefore \text{Using} = \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{770 \times V}{760 \times 313} = \frac{690 \times 95}{760 \times 1000 \times 300}$$

V = 0.0888 L = 88.8 mL

Example 2: At 27°C, an open flask contains air. Determine the temperature at which it should be heated so that:

(a) 1/3rd of the air measured at 27°C escapes out.

(b) 1/3rd of the air measured at the final temperature escapes out.

Sol: (a) Suppose initial moles of gas = n at temperature = 300 K. The gas on heating to TK lose (n/3) moles

∴ Moles of the gas left at temperature T = n – (n/3) = (2n/3)

At constant P and V, $n_1T_1 = n_2T_2$

n × 300 = (2n/3)T

∴ T = 450 K = 177°C

(b) Suppose moles present at TK = n

Moles coming out at TK = n/3

Hence, moles at 300 K should be

n + (n/3) = 4n/3

Therefore, $n_1T_1 = n_2T_2$

n × T = (4n/3) × 300 ∴ T = 400 K = 127°C

Example 3: Calculate the final pressure of O_2 in the following experiment: a collapsed polythene bag of 30 L capacity is partially blown up by the addition of 10 L of N_2 at 0.965 atm at 298 K. Subsequently, enough O_2 is pumped into the bag so that at the temperature of 298 K and external pressure of 0.990 atm, the bag contains a volume of 30 L.

Sol: Initial condition, P_{N_2} = 0.965 atm,

V = 10 L, T = 298 K

O_2 is now introduced to expand the bag fully to 30 L. N_2 also occupies a volume of 30 L at 298 K.

∴ For N_2 alone, new pressure has to be calculated by the following equation:

$P_1V_1 = P_2V_2$

$0.965 \times 10 = P_{N_2} \times 30$

∴ P_{N_2} = 0.322 atm (at 30-L volume)

Total pressure = $P_{O_2} + P_{N_2}$

∴ $P_{O_2} = P_T - P_{N_2} = 0.990 - 0.322 = 0.668$ atm

Example 4: Two bulbs A and B having equal capacity are filled with He and SO_2, respectively, at the same temperature.

(i) If the pressure in the two bulbs is the same, what will be the ratio of rms speed of the molecules of the two gases?

(ii) At what temperature, the speed of SO_2 molecules becomes half of the speed of He

(iii) How does the speed change if the volume of B becomes 4 times that of A at the same temperature?

(iv) How does the speed change if half of the molecules of SO_2 are removed from B?

Sol: (i) For He: $u_{rms} = \sqrt{[(3RT)/M]} = \sqrt{[(3RT)/4]}$

For SO_2: $u_{rms} = \sqrt{[(3RT)/M]} = \sqrt{[(3RT)/64]}$

$$\frac{u_{rms}\text{of He}}{u_{rms}\text{of } SO_2} = 4$$

(ii) Given, urms of SO_2 = $\left(\frac{1}{2}\right)$ u_{rms} of He at 27°C

$$\therefore \sqrt{\frac{3RT}{64}} = \frac{1}{2}\sqrt{\frac{3R \times 300}{4}} \qquad \therefore T = 1200 \text{ K}$$

(iii) $u_{rms} = \sqrt{[(3RT)/M]}$ and, thus, independent of P and V terms. Thus, there is no change in u_{rms} on changing the volume.

(iv) $u_{rms} = \sqrt{[(3RT)/M]}$ and, thus, independent of the number of molecules and therefore no change in u_{rms} by the changing molecules

Example 5: A liquefied petroleum gas (LPG) cylinder weighs 14.8 kg when empty. When full, it weighs 29.0 kg and has a pressure of 2.5 atm. At 27°C, the weight of the full cylinder in the course of its use reduces to 23.2 kg. Calculate the volume of the gas in cubic meters used up under the normal usage conditions and the final pressure inside the cylinder. Assume LPG to be n-butane with a normal boiling point of 0°C.

Sol: Calculate the decrease in the amount which can be used to find the volume.

Decrease in the amount of

LPG = 29.0 – 23.2 = 5.8kg = moles $\frac{5800}{58}$ =100 moles

Volume of 100 moles at a pressure of 1 atm and at a temperature of 300 K = $\frac{nRT}{P}$

$$= \frac{100 \text{ moles} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300\text{K}}{1 \text{ atm}}$$

= 2463 L = 2463 × 10^{-3} m = 2.463 m^3

Final pressure inside the cylinder

As the cylinder contains LPG in equilibrium with its vapors, as long as the temperature remains constant and some LPG is present, pressure will remain constant. As the cylinder still contains LPG = 23.2 – 14.8 = 8.4 kg, the pressure inside the cylinder will be the same, i.e. 2.5 atm.

Example 6: What is the pressure exerted by 1 mole of CO_2 gas at a temperature of 273 K if the van der Waals' constant 'a' = 3.592 dm^6 atm mol^2. Assume that the volume occupied by the CO_2 molecules is negligible.

Sol: According to the van der Waals' equation:

$P + (a/V^2)[V - b] = RT$ (for 1 mole)

If b is negligible, then $[P + (a/V^2)][V] = RT$

or $PV = RT - (a/V)$ or $P = \frac{RT}{V} - \frac{a}{V^2}$

or $V^2P - RTV + a = 0$

$$\text{or } V = \frac{+RT \pm \sqrt{(-RT)^2 - 4Pa}}{2P}$$

As the volume of gas is constant at constant P and T, V can have only one value or discriminant, i.e. 0

or $R^2T^2 - 4\text{ Pa} = 0$

$$\text{or } P = \frac{R^2T^2}{4a} = \frac{(0.0821)^2 \times (273)^2}{4 \times 3.592} = 34.98 \text{ atm}$$

Example 7: A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies a volume of 40 L at 1.00 atm and 400 K. The mixture reacts completely with 130 g of O_2, producing CO_2 and H_2O. Assuming the ideal gas behavior, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture.

Sol: Combustion reactions of ethane and ethene with the calculation of no. of moles by using ideal gas equation is done.

For a gaseous mixture of C_2H_6 and C_2H_4

PV = nRT

$\therefore$ 1 × 40 = n × 0.082 × 400

$\therefore$ n = 1.2195

$\therefore$ Total moles of $C_2H_6 + C_2H_4 = 1.2195$

Let moles of C_2H_6 and C_2H_4 be a and b, respectively

a + b = 1.2195 .... (i)

$C_2H_6 + (7/2)O_2 \rightarrow 2CO_2 + 3H_2O$

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

$\therefore$ Moles of O_2 needed for complete reaction of the mixture = (7a/2) + 3b

$$\therefore\ \frac{7a}{2} + 3b = \left(\frac{130}{32}\right) \qquad \text{.... (ii)}$$

From equations (i) and (ii), a = 0.808, b = 0.4115

$\therefore$ Mole fraction of C_2H_6 = 0.808/1.2195 = 0.66

Mole fraction of C_2H_4 = 0.34

Example 8: The pressure in a bulb dropped from 2000 to 1500 mm of Hg in 47 minutes when the contained O_2 leaked through a small hole. Then, the bulb was completely evacuated. A mixture of O_2 and another gas of molecular weight of 79 in the molar ratio of 1:1 at a total pressure of 4000 mm of Hg was introduced. Calculate the mole ratio of the two gases remaining in the bulb after a period of 74 minutes.

Sol: Pressure of O_2 (at t = 0) = 2000 mm

Let n_1 moles be taken initially

Pressure of O_2 (at 47 min) = 1500 mm

Let n_2 moles be left after 47 min

$\therefore$ For pure O_2: $\frac{P_1}{P_2} = \frac{n_1}{n_2}$

$$\therefore\ \frac{n_1}{n_2} = \frac{2000}{1500} = \frac{4}{3} \qquad \therefore n_2 = \left(\frac{3}{4}\right)n_1$$

$\therefore$ Moles of O_2 diffused in 47 min

= $n_1 - (3n_1/4) = (n_1/4)$

$\therefore$ Mole of O_2 will diffuse in 74 min

$$= \frac{n_1}{4} \times \frac{74}{47} = \frac{74}{188}\, n_1 = 0.3936 \text{ (assume } n_1 = 1)$$

Now, diffusion of O_2 in the mixture also occurs at partial pressure of 2000 mm (the ratio of gas and O_2 being 1: 1)

When both O_2 and the gas diffuse simultaneously at 2000 mm pressure, then for 74 min, $\frac{n_{O_2}}{74} \times \frac{74}{n_g} = \sqrt{\frac{79}{32}}$

$\therefore n_g = n_{O_2} \times \sqrt{(32/79)}$

$= 0.3936 \times \sqrt{(32/79)} = 0.249$

$\therefore$ Moles of O_2 left after 74 min

=1 – 0.3936 = 0.6064

Moreover, moles of the gas left after 74 min

= 1 – 0.249 = 0.7510

$\therefore n_{O_2} : n_g$ = 0.6064: 0.7510:1: 1.236

Example 9: A long rectangular box is filled with Cl_2 (atomic weight 35.45), which is known to contain only Cl^{35} and Cl^{37}. If the box can be divided by a partition and the two types of chlorine molecules put into the two compartments, respectively, determine where should be the partition made if the pressure on both the sides is to be same. Is this pressure the same as the original pressure?

Sol: At constant P and T, the volume of a gas $\propto$ the number of moles, i.e. the mole ratio yields the volume ratio. Thus, the partition should be made in the volume ratio of 3.44: 1. Moreover, pressure at this condition is same as at the original condition since the volume of the box and number of moles along with temperature are constant. Suppose n_1 and n_2 be moles of Cl^{35} and Cl^{37} in the mixture, respectively

$$\text{Average molecular weight} = \frac{35 \times n_1 + 37 \times n_2}{n_1 + n_2}$$

$$\therefore\ 35.45 = \frac{35n_1 + 37n_2}{n_1 + n_2} \text{ or } \frac{n_1}{n_2} = 3.44$$

$\therefore PV_1 = n_1RT;\ PV_2 = n_2RT$

$$\therefore\ \frac{V_1}{V_2} = \frac{n_1}{n_2}$$

Example 10: Determine the critical constants of a gas whose van der Waals' constants are

a = 0.751 L^2 atm mol^{-2} and

b = 0.0226 L mol^{-1}.

Sol: Refer the formulae sheet.

$$P_c = \frac{a}{27b^2} = \frac{0.751\,L^2\ \text{atm mol}^{-2}}{27 \times (0.0226\ \text{L mol}^{-1})^2} = 54.5\ \text{atm}$$

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 0.75\,L^2\ \text{atm mol}^{-2}}{27 \times 0.0821\ \text{L atm K}^{-1}\text{mol}^{-1} \times 0.0226\ \text{L mol}^{-1}}$$

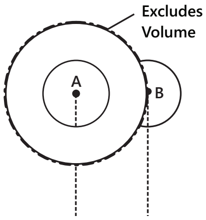
= 120 K

$V_c = 3b = 3 \times 0.0226\ \text{L mol}^{-1} = 0.0678\ \text{L mol}^{-1}$

JEE Advanced/Boards

Example 1: Prove that the excluded volume 'b' is four times the actual volume of gas molecules.

Sol: Let us consider two molecules A and B. Taking the molecules to be spherical, if r is the radius of the molecules, then the distance of the closest approach between the two molecules = 2 r (as shown in Fig.), which is the distance between the centers of their nuclei. As the molecules cannot come closer than the distance 2r, the excluded volume for a pair of molecules = Volume of sphere of radius 2 r.



$$= \frac{4}{3}\pi(2r)^3 = 8 \times \frac{4}{3}\pi r^3$$

∴ The excluded volume per molecule (b)

$$= \frac{1}{2}\left(8\times\frac{4}{3}\pi r^3\right) = 4 \times \frac{4}{3}\pi r^3$$

But $\frac{4}{3}\pi r^3 = v_m$, i.e. the actual volume of the gas molecule

∴ $b = 4v_m$

Example 2: At 27°C, an open vessel is heated until $\frac{3}{5}$ parts of the air in it has been expelled. Assuming that the volume of the vessel remains constant, determine the temperature to which the vessel has been heated.

Sol: Since the vessel is open, pressure and volume remain constant. Therefore, if n_1 moles are present at T_1 and n_2 moles are present at T_2, we can write $PV = n_1RT_1$ and also $PV = n_2RT_2$

Thus, $n_1RT_1 = n_2RT_2$ or $n_1T_1 = n_2T_2$

$$\text{or } \frac{n_1}{n_2} = \frac{T_1}{T_2} \qquad \text{....... (i)}$$

Let us suppose the number of moles of air originally present = n

After heating, the number of moles of air expelled = $\frac{3}{5}$ n

∴ The number of moles left after heating

$$= n - \frac{3}{5}n = \frac{2}{5}n$$

Hence, $n_1 = n$, $T_1 = 300$ K; $n_2 = \frac{2}{5}n$, T_2=?

Substituting in equation (i), we get

$$\frac{n}{\frac{2}{5}n} = \frac{T_2}{300} \text{ or } \frac{5}{2} = \frac{T_2}{300} \text{ or } T_2 = 750 \text{ K}$$

Alternatively, let the volume of the vessel be V, i.e. volume of air initially at 27°C = V

Volume of air expelled = $\frac{3}{5}$ V

∴ The volume of air left at 27°C = $\frac{2}{5}$ V

On heating to T°K, it would become = V

As the pressure remains constant, (vessel being open),

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}, \text{ i.e., } \frac{2/5V}{300K} = \frac{V}{T_2} \text{ or } T_2 = 750 \text{ K}$$

Example 3: A perfectly elastic spherical balloon having a diameter of 0.2 m was filled with hydrogen at sea level. Calculate its diameter when it has risen to an altitude where the pressure is 0.65 atm. (Assume that there is no change in temperature and atmospheric pressure at sea level.)

Sol: If r_1 is the radius of the balloon at sea level, volume of the balloon at sea level = $\frac{4}{3}\pi r_1^3 = \frac{4}{3}\pi(0.1 \text{ m})^3$ i.e. the volume of the gas at sea level (V_1) = $\frac{4}{3}\pi(0.1 \text{ m})^3$

Pressure at the sea level (P_1) = 1 atm

Let the radius of the balloon at altitude be r_2

Volume of the balloon at altitude (V_2) = $\frac{4}{3}\pi r_2^3$

Pressure at the altitude (P_2) = 0.65 arm (given)

As the temperature remains constant, applying Boyle's law $\underset{\text{(At sea level)}}{P_1V_1} = \underset{\text{(At altitude)}}{P_2V_2}$

$$1 \text{ atm} \times \frac{4}{3}\pi(0.1 \text{ m})^3 = 0.65 \text{ atm} \times \frac{4}{3}\pi r_2^3 \qquad \text{or}$$

$$r_2^3 = \frac{(0.1\text{m})^3}{0.65} = 1.54 \times 10^{-3} \text{ m}^3$$

∴ $r_2 = (1.54 \times 10^{-3})^{1/3}$ m = 0.1154 m

∴ The diameter of the balloon at altitude = 2 × 0.1154 m = 0.2308 m

Example 4: Assuming oxygen molecule to be spherical in shape, find out the volume of a single molecule of oxygen if its radius is 150 pm. Calculate the percentage of empty space in one mole of the gas at STP.

Sol: As oxygen molecule is spherical, volume of one molecule = $\frac{4}{3}\pi r^3 = \frac{4}{3} \times \frac{22}{7}(150 \times 10^{-10} \text{ cm})^3$

$= 1.41 \times 10^{-23}$ cm^3

To calculate the empty space in 1 mole of O_2 molecules, let us first calculate the volume occupied by 1 mole of the molecules, i.e. 6.022×10^{23} molecules, which will be

= $(6.022 \times 10^{23}) \times (1.41 \times 10^{-23}$ cm3) = 8.49 cm^3.

Volume occupied by 1 mole of molecules at STP = 22,400 cm^3

$\therefore$ Empty space = 22400 – 8.49cm^3 = 22391.51 cm^3

$$\% \text{ of empty space} = \frac{22391.51}{22400} \times 100 = 96.96\%$$

Example 5: A spherical balloon having a diameter of 21 cm is to be filled with hydrogen at NTP from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.82 L of water, then calculate the number of balloons that can be filled up.

Sol: To find the no. of balloons, volume of one balloon can be equated with the available gas to be filled.

Volume of the balloon

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

Volume of the cylinder = 2.82 L = 2820 cm^3

Pressure = 20 atm

Temperature = 300 K

Converting this to the volume at NTP, we get

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \therefore \frac{20 \times 2820}{300} = \frac{1 \times V_2}{273}$$

or V_2 = 51324 cm^3

When the pressure in the cylinder is reduced to 1 atm, no more H_2 will be released and thus 2820 cm^3 of H_2 will be left in it. Therefore, the volume of H_2 used in filling the balloons

= 51324 – 2820 cm^3

= 48504 cm^3

Number of balloons filled = 48504/4851 = 10

Example 6: A liquefied petroleum gas (LPG) cylinder weighs 14.8 kg when empty. When full, it weights 29.0 kg and has a pressure of 2.5 atm. At 27°C, the weight of the full cylinder in the course of its use has reduced to 23.2 kg. Calculate the volume of the gas in cubic meters used up under the normal usage conditions and the final pressure inside the cylinder. Assume LPG to be n-butane with a normal boiling point of 0°C.

Sol: Weight of butane in the cylinder

= 29.0 – 14.8 = 14.2 kg = 14.2×10^3 g

P = 2.5 atm, T = 300 K, molecular weight of butane = 58

$$\therefore PV = \frac{w}{m} RT$$

$$2.5 \times V = \frac{14.2 \times 10^3}{58} \times 0.0821 \times 300$$

V = 2.4120×10^3 L = 2.4120 m^3

This is the volume of the cylinder or the volume of the gas.

Now, the weight of the gas left after use = 23.2 – 14.8

= 8.4 kg = 8.4×10^3 g

Volume remains constant

Using PV = (w/m) RT

$$P \times 2.412 \times 10^3 = \frac{8.4 \times 10^3}{58} \times 0.0821 \times 300$$

$\therefore$ Pressure (P) of the gas left in cylinder = 1.48 atm

Now, pressure of the gas given out = 1 atm

Weight of the gas given out = (29.0 – 23.2) kg

= 5.8 kg = 5.8×10^3 g

Therefore, the volume of gas given out under these conditions is given by the following equation:

$$\therefore 1 \times V = \frac{5.8 \times 10^3}{58} \times 0.0821 \times 300$$

$\therefore$ V = 2463 L = 2.463 m^3

Example 7: If the volume occupied by CO_2 molecules is negligible, then find out the pressure exerted by 1 mole of CO_2 gas at 273 K (a = 3.592 atm L^{-2} mol^{-2})

Sol: Using Vander Waal's equation, get a quadratic equation from which the pressure can be found.

For 1 mole, $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

If b is negligible, then $\left(P + \frac{a}{V^2}\right) V = RT$

or $P = \frac{RT}{V} - \frac{a}{V^2}$ or $PV^2 - RTV + as = 0$

This equation is found to be quadratic in V. Thus,

$$V = \frac{+RT \pm \sqrt{R^2T^2 - 4aP}}{2P}$$

As V can have only one value at P and T, we must have

$R^2T^2 - 4aP = 0$ or $R^2T^2 = 4aP$

$$\text{or } P = \frac{R^2T^2}{4a}$$

$$= \frac{(0.0821\ \text{L atm K}^{-1}\text{mol}^{-1})^2(273\text{K})^2}{4 \times 3.592 \text{atm L}^{-2}\ \text{mol}^{-2}} = 34.96 \text{ atm}$$

Example 8: (i) When a pressure deodorant can is used for a few seconds, the can tends to become cooler. Why?

(ii) When the ping pong ball, used as a toy by children, gets dented without being punctured, what do we do to regain the original shape and why?

(iii) Bottles and beer or soda cans have a label on them stating 'Store in a cool, dry place.' Why?

(iv) In winter, inflated football gets deflated. Why?

If you live in a centrally heated apartment and on a chilly winter day, you inflate a football inside your apartment and then go out to play, the football seems deflated. Why?

(v) Why hot air is filled in balloons for meteorological observations?

Sol: (i) On spraying the can, the liquid spray of the can is released. Thus, the pressure inside decreases a bit. As the can's volume does not change, the temperature falls.

(ii) We place the dented ping-pong ball in warm water to regain the original shape. As the temperature inside increases (i.e. air inside gets warmer), the pressure inside also increases. As a result, the dent gets removed.

(iii) The reason is that these cans have a lot of artificial pressure stored inside them. When exposed to direct sunlight/heat, the pressure inside the cans rises because the volume remains constant. The can explodes when the pressure exceeds a particular limit.

(iv) When the ball is brought outside, the temperature drops. As a result, the pressure of the air inside the football also drops, making the ball look deflated.

(v) When air is heated, it expands, resulting in the decrease of its density. Hence, hot air is lighter than atmospheric air, which helps the balloon to rise up.

Example 9: (i) The magnitude of surface tension of a liquid depends on the attractive forces between the molecules. Arrange the following in the increasing order of surface tension:

Water, alcohol (C_2H_5OH) and hexane [$CH_3(CH_2)_4CH_3$].

(ii) The van der Waals' constants for two gases are as follows:

Gas	a (atm L² mol⁻²)	b (L mol⁻¹)
X	1.39	0.0391
Y	3.59	00427

Which of the gases is more easily liquefiable and which has a greater molecular size?

(iii) At the same temperature, liquid is transferred from a smaller vessel to a bigger vessel. Determine the effect on the vapor pressure?

Sol: (i) In hexane, attractive forces are minimum (only London forces). Hydrogen bonding in H_2O is stronger as compared with the hydrogen bonding in C_2H_5OH. Thus, the order of surface tension is hexane < alcohol < water.

(ii) Greater the value of 'a,' more easily the gas gets liquefied. Also, greater the value of 'b', greater is the molecular size. Thus, gas Y will be more easily liquefiable and will have a greater molecular size.

(iii) No effect since it depends only on the nature of the liquid and temperature.

Example 10: At NTP, a mixture of 1 L of O_2 and 1 L of H_2 is taken in a vessel of 2-L capacity. The gases are allowed to combine to form water.Determine (a) the moles and weight of water formed, (b) the amount of gas left in the vessel, (c) the total pressure if the vessel is heated to 100°C and (d) mole of O_2 used for the formation of water.

Sol: Frame the reaction and lay down the values of the individual reacting species. Apply ideal gas equation to find out moles and to solve the volume of the species.

The given reaction is as follows:

$2H_2 + O_2 \longrightarrow 2H_2O$

Volume before 1 1 0

the reaction (in liters)

Volume after 0 0.5 1

the reaction (liters)

(a) At NTP, moles of H_2O formed = Moles of H_2 used

$$= \frac{PV}{RT} = \frac{1 \times 1}{0.0821 \times 273} = 4.46 \times 10^{-2}$$

∴ The weight of H_2O formed

$= 4.46 \times 10^{-2} \times 18 = 8.03 \times 10^{-1}$ g

(b) Total moles of O_2 left $= \dfrac{1 \times 0.5}{0.0821 \times 273} = 2.23 \times 10^{-2}$

∴ The weight of O_2 left $= 2.23 \times 10^{-2} \times 32 = 0.7136$ g

(c) On heating to a temperature of 100°C, H_2O exists as vapor

∴ Total moles present at a temperature of 100°C

= Moles of H_2O + Moles of O_2

$= 4.46 \times 10^{-2} + 2.23 \times 10^{-2}$

$= 6.69 \times 10^{-2}$ K

Volume of the vessel = 2 L, T = 373 K

$$\therefore P = \frac{nRT}{V} = \frac{6.69\times10^{-2}\times0.0821\times373}{2} = 1.02 \text{ atm}$$

(d) Volume of O_2 used for the formation of H_2O = 0.5 L

$\therefore$ Moles of O_2 used for the formation of H_2O at

$$\text{NTP} = \frac{0.5}{22.4} = 2.23 \times 10^{-2}$$

JEE Main/Boards

Exercise 1

Q.1 Calculate the Kinetic energy in joules of the molecules in 8.0 g of methane gas at 27°C.

Q.2 3.7 g of a gas at 25°C occupied the same volume as 0.184 g of hydrogen at 17°C and at the same pressure. What is the molecular weight of the gas?

Q.3 Calculate the density of NH_3 gas at 30°C and 5 atmosphere pressure.

Q.4 A dessicator of internal volume of 1 litre and containing nitrogen at 1 atmosphere pressure is partially evacuated to a final pressure of 7.6 mm of Hg, while the temperature remains constant what is the volume of the gas at this stage.

Q.5 Calculate the volume of 6.0 g of hydrogen at 1.5 atmosphere and 273°C

Q.6 When 3.2 g of sulphur is vaporized at 450°C and 723 mm pressure the vapour occupies a volume of 780 mL. What is the molecular formula of sulphur vapour under these condition?

Q.7 The ratio of rates of diffusion of gases A and B is 1:4. If the ratio of their masses present in the mixture is 2:3 calculate the ratio of their mole fractions.

Q.8 Calculate the volume occupied by 5 g of acetylene gas at 50°C and 740 mm pressure.

Q.9 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially?

Q. 10 The composition of equilibrium mixture ($Cl_2 - 2Cl$) which is attained at 1200°C, is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.8 mm. Hg pressure, the mixture effuses 1.16 times as fast as Krypton effuses under the same condition. Calculate the fraction of chlorine molecules dissociated into atoms (At. wt. of Kr = 84).

Q.11 20 dm^3 of SO_2 diffuse through a porous partition in 60 seconds. What volume of O_2 will diffuse under similar condition in 30 seconds?

Q.12 Calculate the root mean square speed of ozone kept in a closed vessel at 20°C and 82 cm mercury pressure.

Q.13 Oxygen is present in a 1.0 litre flask at pressure 7.6×10^{-10} mm Hg. Calculate the no. of oxygen molecules in the flask at 0°C.

Q.14 Calculate the volume occupied at 27°C and 2 atmosphere of the gas evolved from 2 mL of solid carbon dioxide. Given that the density of solid carbon dioxide is 1.53 g/mL.

Q.15 Calculate the relative rate of diffusion for $^{235}UF_6$ and $^{238}UF_6$ gaseous form.

Q.16 The pressure exerted by 12 g of an ideal gas at temperature t°C in a vessel of volume V litres is one atmosphere. When the temperature is increased by 10° at the same volume, the pressure increased by 10%. Calculate the temperature t and volume V. (Molecular weight of the gas is 120).

Q.17 A mixture in which the mole ratio of H_2 and O_2 is 2: 1 is used to prepare water by the reaction

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}.$$

The total pressure in the container is 0.8 atmosphere at 20°C before the reaction. Determine the final pressure at 120°C after the reaction assuming 80% yield of water.

Q.18 An open vessel at 27°C is heated until 3/5 of the air in it has been expelled. Assuming the volume of the vessel to be constant find the temperature to which the vessel was heat.

Q.19 When 2 g of a gaseous substance (A) is introduced into an initially evacuated flask at 25°C, the pressure is found to be 1 atmosphere 3.0 g of another gas (B) is then added to it at the same temperature and pressure. The final pressure is found to be 1.5 atmosphere. Assuming ideal gas behaviour calculate the ratio of molecular weights of (A) and (B).

Q.20 At room temperature ammonia gas at one atmospheric pressure and hydrogen chloride at P atmosphere are allowed to effuse through identical pinholes from opposite ends of a glass tube of 1 meter length and of uniform cross-section. NH_4Cl is first formed at a distance of 60 cm from the end through which HCl gas is seat in. Find out the value of P

Q.21 A plant virus is found to consist of uniform cylindrical particles of 150 Å m diameter and 500 Å long. The specific volume of virus is 0.75 cm^3/g. If the virus is considered to be a single particle find its molecular weight.

Q.22 The mass of molecule A is twice the mass of molecule B. The r.m.s. speed of A is twice the r.m.s. speed of B. If two samples of A and B contain same no of molecules. What will be the ratio of P of two samples?

Q.23 Two glass bulbs of equal volume are connected by a narrow tube and filled with a gas at 0°C and pressure of 76 cm of Hg. One of the bulb is then placed in a water bath maintained at 62°C. What is the new value of the pressure inside the bulbs the volume of the connecting tube is negligible.

Q.24 A column of Hg of 10 cm in length is contained in the middle of a narrow 1 m long tube which is closed at both ends. Both the halves of the tube contained air at a pressure of 76 cm of Hg. By what distance will the column of Hg be displaced if the tube is held vertical?

Q.25 Using Vander Waal's equation, calculate the constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atmosphere at a temperature of 300 K. The value of b is 0.05 litre mol^{-1}.

Q.26 An evacuated glass vessel weighs 50.0 g when empty 148.0 g when filled with a liquid of density 0.98 gmL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.

Q.27 Calculate the total pressure in a 10 litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour for gases.

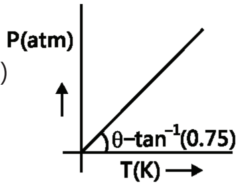
Exercise 2

Single Correct Choice Type

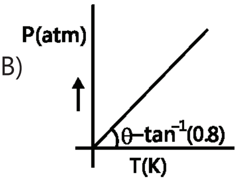
Q.1 Gas A(1 mol) dissociates in a closed rigid container of volume 0.16 lit. as per following reaction $2A(g) \longrightarrow 3B(g) + 2C(g)$

If degree of dissociation of A is 0.4 and remains constant in entire range of temperature, then the correct P vs T graph is [Given R = 0.08 lit-atm mol/K]

(A)



(B)



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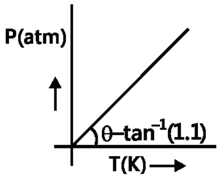
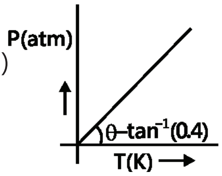


(D)



Q.2 Calculate the ratio of rate of effusion of O_2 and H_2 from a container containing 16 gm O_2 and 2gm H_2:

(A) 1: 8 (B) 8: 1 (C) 1: 4 (D) 4: 1

Q.3 Kinetic energy of one mole of CO_2 at 'T' K is:

(A) 3 RT (B) 2/3 RT

(C) 3/2 RT (D) None of these

Q.4 The mean kinetic energy of 1 mole of CO_2 at 300 K is E. The average kinetic energy at 1500 K will be:

(A) E/5 (B) 5 E (C) 3/5 E (D) E

Q.5 At what temperature the RMS velocity of oxygen molecules is equal to that of SO_2 at 300 K?

(A) +123°C (B) –123°C

(C) 27°C (D) 600 K

Q.6 Temperature at which most probable speed of O_2 becomes equal to root mean square speed of N_2 is [Given: N_2 at 427°C]:

(A) 732 K (B) 1200 K

(C) 927 K (D) 800 K

Q.7 A rigid container containing 10 gm gas at some pressure and temperature. The gas has been allowed to escape (do not consider any effusion or diffusion) from the container due to which pressure of the gas becomes half of its initial pressure and temperature become (2/3rd of its initial. The mass of gas (in gms) escaped is:

(A) 7.5 (B) 1.5 (C) 2.5 (D) 3.5

Q.8 If the absolute temperature and pressure of a gas are doubled, its volume would become:

(A) Doubled

(B) Halve

(C) Increases four times

(D) Remains the same

Q.9 Two gases contained separately in flasks of equal pressures of 1 atmosphere each. What will be the resultant pressure if the flasks are connected?

(A) 2 atmosphere (B) 1/2 atmosphere

(C) 1 atmosphere (D) None of these

Q.10 At very low pressure, the Vander Waal's equation for one mole is written is:

(A) $PV - pb = RT$ (B) $PV + a = RT$

(C) $PV = RT$ (D) $(P + a/V^2)(V) = RT$

Q.11 A gas cylinder contains 0.3 mol of N_2, 0.2 mol of O_2 and 0.5 mol of helium. If the total pressure is P atmospheres, what will be the partial pressure of nitrogen?

(A) P/5 atm (B) 0.3 × P × 760 mm

(C) $\frac{P}{0.3}$ × 760 mm (D) $\frac{P}{0.3}$ × atm

Q.12 10 g each of sulphur dioxide, phosphine and hydrogen are kept in three flasks. Decreasing order of number of atoms is:

(A) Phosphine, sulphur dioxide, hydrogen

(B) Hydrogen, phosphine, sulphur dioxide

(C) Sulphur dioxide, phosphine, hydrogen

(D) Hydrogen, sulphur dioxide, phosphine

Q.13 Pressure of a real gas is less than that of ideal gas due to:

(A) Increase in the number of collisions

(B) Intermolecular forces of attractions

(C) Increase in the kinetic energy of molecules

(D) Finite size of the molecules

Q.14 Values of Vander Waal's constant 'a' for three gases A, B and C are 5.6, 3.6 and 2.4 respectively. The increasing order of their ease of liquefaction will be:

(A) A, B, C (B) C, B, A (C) B, A, C (D) B, C, A

Q.15 The volume of 6 g hydrogen at 1.5 atm and 273°C is:

(A) 89.65 mL (B) 0.895 mL

(C) 8.95 mL (D) None of these

Q.16 A gas cylinder containing cooking gas can withstand a pressure at 14.9 atm. The pressure gauge of the cylinder indicates 12 atm. at 27°C. Due to a sudden fire in the building its temperature starts rising. At what temperature will be cylinder explode?

(A) 372.5 K (B) 3.725 K

(C) 37.25 K (D) None of these

Q.17 When 2 g of a gas A is introduced into an evacuated flask kept at 25°C, the pressure is found to be one atmosphere. If 3 g of another gas B is then added to the same flask, the total pressure becomes 1.5 atmosphere. Assuming ideal gas behaviour, calculate the ratio of molecular wt. MA: MB.

(A) 3: 1 (B) 1: 4 (C) 1: 3 (D) None of these

Q.18 Two vessels of the same capacity and at the same temperature are filled with 44 g of hydrogen gas in one and 44 g of CO_2 in the other. If the pressure of CO_2 in the second container is 1 atm that of hydrogen in the first container would be -

(A) 1 atm (B) 22 atm (C) 10 atm (D) 44 atm

Q.19 Select the correct option(s) for an ideal gas:

(A) Most probable speed increases with increase in temperature

(B) Fraction of particles moving with most probable speed increases with increase in temperature

(C) Fraction of particles moving with most probable speed are more for Cl_2 than H_2 under similar condition of T, P & V

(D) Most probable speed is more for Cl_2 than H_2 at same temperature

Previous Years' Questions

Q.1 A mono-atomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas? ***(2006)***

(A) $\frac{4R}{2}$ (B) $\frac{3R}{2}$ (C) $\frac{5R}{2}$ (D) 0

Q.2 For an ideal gas number of moles per litre in terms of pressure is P gas constant R and temperature T is: ***(2006)***

(A) PT/R (B) PRT (C) P/RT (D) RT/P

Q.3 An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If Ti is the initial temperature and Tf is the final temperature, which of the following statements is correct: ***(1992)***

(A) $(T_f)_{irrev} > (T_f)_{rev}$

(B) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(C) $(T_f)_{irrev} = (T_f)_{rev}$

(D) $T_f = T_i$ for both reversible and ineversible processes

Q.4 X mL of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical condition is: ***(2006)***

(A) 10 seconds: He (B) 20 seconds: O_2

(C) 25 seconds: CO (D) 55 seconds: CO_2

Q.5 Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is: ***(2007)***

(A) $\frac{2}{3}$ (B) $\frac{1}{3} \times \frac{273}{298}$ (C) $\frac{1}{3}$ (D) $\frac{1}{2}$

Q.6 If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established:

(Given: Vapour pressure of H_2O at 300 K is 3170 Pa; R = 8.314 JK^{-1} mol^{-1}) ***(2010)***

(A) 1.27×10^{-3} mol (B) 5.56×10^{-3} mol

(C) 1.53×10^{-2} mol (D) 4.46×10^{-2} mol

Q.7 At constant volume, for a fixed number of moles of a gas, the pressure of the gas increases with increase in temperature due to: ***(1992)***

(A) Increase in the average molecular speed

(B) Increased rate of collision amongst molecules

(C) Increase in molecular attraction

(D) Decrease in mean free path

Q.8 The ratio between the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is: ***(1996; 2006)***

(A) 4 (B) 2 (C) 1 (D) ¼

Q.9 Which one of the following statements is NOT true about the effect of an increase in temperature on the distribution of molecular speeds in a gas ***(2005)***

(A) The most probable speed increases

(B) The fraction of the molecules with the most probable speed increases

(C) The distribution becomes broader

(D) The area under the distribution curve remains the same as under the lower temperature.

Q.10 Vander Waal's equation of state for a non-ideal gas, the term that accounts for intermolecular forces is: ***(1998; 1990)***

(A) (V – b) (B) $(RT)^{-1}$ (C) $\left(P + \frac{a}{V^2}\right)$ (D) RT

Q.11 When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules: ***(1984, 89)***

(A) Are above the inversion temperature

(B) Exert no attractive force on each other

(C) Do work equal to loss in kinetic energy

(D) Collide without loss of energy

Q.12 In Vander Waal's equation of state of the gas law, the constant 'b' is a measure of: ***(2004)***

(A) Volume occupied by the molecules

(B) Intermolecular attraction

(C) Intermolecular repulsions

(D) Intermolecular collisions per unit volume

Q.13 The compression factor (compressibility factor) for 1 mole of a Vander Waal's gas at 0°C and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the Vander Waal's constant 'a': ***(2004)***

(A) 0.253 $L^2\ mol^{-2}$ atm
(B) 0.53 $L^2\ mol^{-2}$ atm
(C) 1.83 $L^2\ mol^{-2}$ atm
(D) 1.253 $L^2\ mol^{-2}$ atm

Q.14 As the temperature is raised from 20°C to 40°C the average kinetic energy of neon atoms changes by a factor of which of the following ***(2004)***

(A) 313/293
(B) $\sqrt{(313/293)}$
(C) 1/2
(D) 2

Q.15 If C_1, C_2, C_3........ represent the speeds of n_1, n_2, n_3........ molecules, then the root mean square speed is ***(1993)***

(A) $\left(\dfrac{n_1C_1^2 + n_2C_2^2 + n_3C_3^2 + ...}{n_1 + n_2 + n_3 + ...}\right)^{1/2}$

(B) $\dfrac{(n_1C_1^2 + n_2C_2^2 + n_3C_3^2 + ...)^{1/2}}{n_1 + n_2 + n_3 + ...}$

(C) $\dfrac{(n_1C_1^2)^{1/2}}{n_1} + \dfrac{(n_2C_2^2)^{1/2}}{n_2} + \dfrac{(n_3C_3^2)^{1/2}}{n_3} + ...$

(D) $\left[\dfrac{(n_1C_1 + n_2C_2 + n_3C_3 + ...)^2}{(n_1 + n_2 + n_3 + ...)}\right]^{1/2}$

Q.16 `a' and `b' are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because ***(2011)***

(A) a and b for Cl_2 < a and b for $C_2\ H_6$

(B) a for Cl_2 < a for C_2H_6 but b for Cl_2 > b for C_2H_6

(C) a for Cl_2 > a for C_2H_6H but b for Cl_2 < b for C_2H_6

(D) a and b for Cl_2 > a and b for C_2H_6

Q.17 For gaseous state, if most probable speed is denoted by C*, average speed by $\bar{C}$ and mean square speed by C, then for a large number of molecules the ratios of these speeds are : ***(2013)***

(A) C*: $\bar{C}$: C = 1.225: 1.128: 1

(B) C*: $\bar{C}$: C = 1.128: 1.225: 1

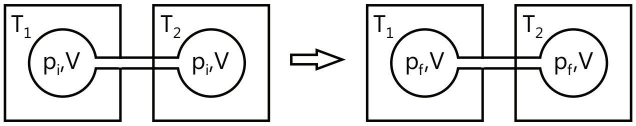
(C) C*: $\bar{C}$: C = 1: 1.128: 1.225

(D) C*: $\bar{C}$: C = 1: 1.225: 1.128

Q.18 If Z is a compressibility factor, van der Waals equation at low pressure can be written as ***(2014)***

(A) $Z = 1 + \dfrac{RT}{Pb}$
(B) $Z = 1 - \dfrac{a}{VRT}$
(C) $Z = 1 - \dfrac{Pb}{RT}$
(D) $Z = 1 + \dfrac{Pb}{RT}$

Q.19 Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure p_i and temperature T_1 are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to T_2. The final pressure p_f is: ***(2016)***



JEE Advanced/Boards

Exercise 1

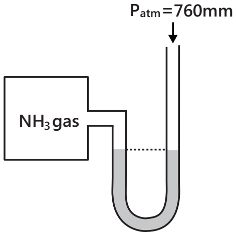
Q.1 Automobile air bags are inflated with N_2 gas which is formed by the decomposition of solid sodium azide (NaN_3). The other product is Na-metal. Calculate the volume of N_2 gas at 27°C and 756 Torr formed by the decomposing of 125 gm of soda azide.

Q.2 3.6 gm of an ideal gas was injected into a bulb of internal volume of 8L at pressure P atmp and temp T-K. The bulb was then placed in a thermostat maintained at (T+15) K 0.6 gm of the gas was let off to keep the original pressure. Find P and T if mol weight of gas is 44.

Q.3 While resting, the average human male use 0.2 dm^3 of O_2 per hour at 1 atm & 273 K for each kg of body mass. Assume that all this O_2 is used to produce energy by oxidizing glucose in the body. What is the mass of glucose required per hour by a resting male having mass 60 kg. What volume, at 1 atm & 273 K of CO_2 would be produced.

Q.4 An ideal gas is at a temperature of 200 K & at a pressure of 8.21 atm. It is subjected to change in volume by changing amount of the gas & a graph of n_2 vs V_2 (litre1) is plotted Is slope constant? If yes, calculate its value else justify why is not constant.

Q.5 A manometer attached to a flask contains, NH_3 gas have no difference in mercury level initially as shown in diagram After the sparking into the flask, it have difference of 19 cm in mercury level in two columns. Calculate % dissociation.



Q.6 1.0×10^{-2} kg of hydrogen and 6.4×10^{-2} kg of oxygen are contained in a 10×10^{-3} m^3 flask at 473 K. Calculate the total pressure of the mixture. If a spark ignites the mixture. What will be the final pressure?

Q.7 Calculate relative rate of effusion of SO_2 to CH_4 under given condition

(i) Under similar condition of pressure & temperature

(ii) Through a container containing SO_2 and CH_4 in 3: 2 mass ratio

(iii) If the mixture obtained by effusing out a mixture $(n_{SO_2} / n_{CH_4} - 8/1)$ for three effusing steps.

Q.8 Pure O_2 diffuses through an aperture in 224 sec, whereas mixture of O_2 and another gas containing 80% O_2 takes 234 sec to effuse out same volume what is the molecular weight of the gas?

Q.9 Find the number of diffusion steps required to separate the isotopic mixture initially containing some amount of H_2 gas and 1 mol of D_2 gas in a container of 3 lit capacity maintained at 24.6 atm & 27°C to the final mass ratio. $\left(\frac{W_{D_2}}{W_{H_2}}\right)$ Equal to $\frac{1}{4}$

Q.10 An iron cylinder contains helium at a pressure of 250 k pa and 27°C. The cylinder can withstand a pressure of 1×10^4 pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. [Melting point of cylinder = 1800 k]

Q.11 Calculate U of molecules of H_2 at 1 atm if density of H_2 is 0.00009 g/cc.

Q.12 A bulb of capacity 1 dm^3 contains 1.03×10^{23} H_2 molecules & external pressure exerted by these molecules is 101.325 k Pa. Calculate the average square molecular speed and the temperature.

Q.13 The density of CO at 273 K and 1 atm is 1.2504 kg m^{-3}. Calculate (a) root mean square speed (b) the average speed and (c) most probable speed.

Q.14 Calculate the fraction of N_2 molecules at 101.325 k Pa and 300 K whose speeds are in the range of $u_{mp} - 0.005\ u_{mp}$ to $u_{mp} + 0.005\ u_{mp}$.

Q.15 What is the ratio of the number of molecules having speeds in the range of $2u_{mp}$ and $2u_{mp} + du$ to the number of molecules having speeds in the range of u_{mp} and $u_{mp} + du$?

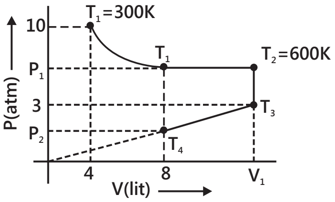
Q.16 H_2 gas is kept inside a container A and container B each having volume 2 litre under different conditions which are described below. Determine the missing values with proper unit. [R = 8 J mol^{-1} K^{-1} and NA = 6×10^{23}, N = No. of molecules]

Parameter	**Container A**	**Container B**
P	(i) -------	1 atm
T	300 K	600 K
N	6×10^{23}	(ii) -------
Total Average KB	(iii) -------	(iv) -------
Ratio U_{mp}	(v) -------	
Ratio Z_n	(vi) -------	

Q.17 A mixture of hydrogen and helium is prepared such that the number of wall collisions per unit time by molecules of each gas is the same. Which gas has a higher concentration?

Q.18 The mean free path of the molecule of a certain gas at 300 K is 2.6×10^{-5} m . The collision diameter of the molecule is 0.26 mm. Calculate (a) pressure of the gas, and (b) number of molecules per unit volume of the gas.

Q.19 Fixed mass of a gas is subjected to the changes as shown in diagram, calculate T_3, T_4, T_1, P_2 and V_1 as shown is diagram. Considering gas obeys PV = nRT equation.



Q.20 A balloon containing 1 mole of air at 1 atm initially is filled further with air till pressure increases to 3 atm. The initial diameter of the balloon is 1 m and the pressure at each state is proportion to diameter of the balloon. Calculate-

(a) No. of moles of air added to change the pressure from 1 atm to 3 atm.

(b) Balloon will burst if either pressure increases to 7 atm or volume increases to 36 πm^3. Calculate the number of moles of air that must be added after initial condition to burst the balloon.

Q.21 One mole of $NH_4Cl(s)$ is kept in an open container & then covered with a lid. The container is now heated to 600 K where all $NH_4Cl(s)$ dissociates into NH_3 & HCl(g). If volume of the container is 24.63 litres, calculate what will be the final pressure of gases inside the container. Also find whether the lid would stay or bounce off if it can with stand a pressure difference of 5.5 atm.
Assume that outside air is at 300 K and 1 atm pressure.

Q.22 Calculate the value of σ, λ, z_1 and z_{11} for nitrogen molecules at 25°C and at pressure of 10^{-3} mm Hg. Given that b for nitrogen is 39.1 $cm^3\ mol^{-1}$

Q.23 A gas present in a container connected to frictionless, weightless piston operating always at one atmosphere pressure such that it permits flow of gas outside (with no adding of gas.). The graph of n vs T (Kelvin) was plotted & was found to be a straight line with Co-ordinates of extreme points as (300, 2) & (200, 3). Calculate

(i) Relationship between n & T

(ii) Relationship between V & T

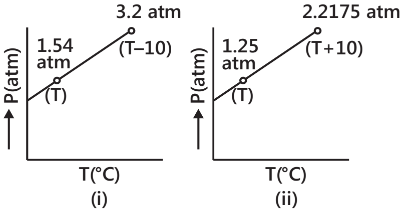
(iii) Maxima or minima value of 'V'

Q.24 A compound exists in the gaseous state both as a monomer (A) and dimer (A_2). The molecular weight of the monomer is 48. In an experiment, 96 g of the compound was confined in a vessel of volume 33.6 litres and heated to 273°C. Calculate the pressure developed, if the compound exists as a dimer to the extent of 50 per cent by weight, under these conditions, (R = 0.082)

Q.25 A closed vertical cylinder is divided into two parts by a frictionless piston, each part contains 1 mole of air. At 27°C the volume of the upper part is 4 times than that of the lower part. Calculate the temperature when volume of the upper part will be three times than that of the lower part.

Q.26 You are told to prepare a closed experimental environment (a box) for student mice. The box volume will be 294 liters (about 10 ft^3) and the entire air volume will be changed every minute. The relative humidity of the air entering the box is to be controlled at 40% at 21°C. What weight of H_2O must be added to the flow of dry air per minute? (Equilibrium vapour pressure for H_2O at 21°C ≅ 19 torr). (R = 0.082 liter atm $mole^{-1}\ deg^{-1}$ Mol wt: H_2O = 18)

Q.27 A closed vessel of known volume containing known amount of ideal gaseous substance 'A' was observed for variation of pressure with temperature. The expected graph was to be like as in



(i) (ii)

(i) However actual observations revealed the graph to be like. (ii) The deviation was attributed to polymerisation of gas molecules as $nA(g)\ IA_n(g)$. If it known that the above reaction gives only 50% yield

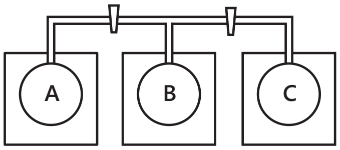
(a) Calculate the ratio of $\frac{n_{experiment}}{n_{theoretical}}$ (where $n_{exp.}$ = Total no. of gaseous mole actually present $n_{theoretical}$ = Total no. of mole original taken,

(b) Find the value of n to which the gas A is being polymerized into

Q.28 A mixture of CH_4 & O_2 is used as an optimal fuel if O_2 is present in thrice the amount required theoretically for combustion of CH_4. Calculate number of effusions steps required to convert a mixture containing 1 part of CH_4 in 193 parts mixture (parts by volume). If calorific value (heat evolved when 1 mole is burnt) of CH_4 is 100 cal/mole & if after each effusion 90% of CH_4 is collected, find out what initial mole of each gas in initial mixture required for producing 1000 cal of energy after processing. [Given $(0.9)^5 = 0.6$]

Q.29 A 50 litre vessel is equally divided into three parts with the help of two stationary semi permeable membrane (SPM). The vessel contains 60 g H_2 gas in the left chamber 160gO_2 in the middle & 140 g N_2 in the right one. The left SPM allows transfer of only H_2 gas while the right one allows the transfer of both H_2 & N_2. Calculate the final ratio of pressure in the three chambers.

Q.30 The apparatus shown consists of three temperature jacketed 1 litre bulbs connected by stop cocks. Bulb A contains a mixture of $H_2O(g)$, $CO_2(g)$ and $N_2(g)$ at 27°C and a total pressure of 547.2 mm Hg. Bulb B is empty and is held at a temperature -23°C. Bulb C is also empty and is held at a temperature of 173°C. The stopcocks are closed and the volumes of limes connecting the bulbs is zero. Given. $CO_2(g)$ converted into $CO_2(s)$ at –78°, N(g) convened into N(s) at –196°C & $H_2O(g)$ converted into $H_2O(s)$ at 0°C.



[Use R = 0.08 atm- litre/mole. K]

(a) The stopcock between A & B is opened and the system is allowed to come to equilibrium. The pressure in A & B is now 228 mmHg. What do bulbs A & B contain?

(b) How many moles of H_2O are in system?

(c) Both stopcocks are opened and the system is again allowed to equilibrium. The pressure throughout the system is 45.6 mmHg. What do bulbs A, B and C contain?

Exercise 2

Single Correct Choice Type

Q.1 The number of effusion steps required to convert a mixture of H_2 and O_2 from 240: 1600 (by mass) to 3072: 20 (by mass) is:

(A) 2 (B) 4 (C) 5 (D) 6

Q.2 Consider the following pairs of gases A and B.

	A	B
(a)	CO	N_2
(b)	O_2	O_3
(c)	$^{235}UF_6$	$^{238}UF_6$

Relative rates of effusion of gases A to B under similar condition in the order:

(A) a < b < c (B) a < c < b

(C) a > b > c (D) a > c > b

Q.3 The pressure of mixture of equal weights of two gases of molecular weight 4 and 40 is 1.1 atm. The partial pressure of the lighter gas in the gas mixture is:

(A) 0.55 atm (B) 0.11 atm

(C) 1 atm (D) 0.1 atm

Q.4 The density of gas A is twice that of B at the same temperature the molecular weight of gas B is thrice that of A. The ratio of pressure of gas A and gas B will be:

(A) 1: 6 (B) 7: 8 (C) 6: 1 (D) 1: 4

Q.5 For the reaction $2NH_3(g)\rightarrow N_2(g) + 3H_2(g)$, what is the % of NH_3 converted if the mixture diffuses twice as fast as that of SO_2 under similar conditions:

(A) 3.125% (B) 31.25%

(C) 6.25% (D) 62.5%

Q.6 A gaseous reaction, $3A \longrightarrow 2B$ is carried out in a 0.0821 litre closed container initially containing 1 mole of gas A. After sufficient time a curve of P(atm) vs T(K) is plotted and the angle with x-axis was found to be 42.95°. The degree of association of gas A is [Given: tan 42.95 = 0.8]

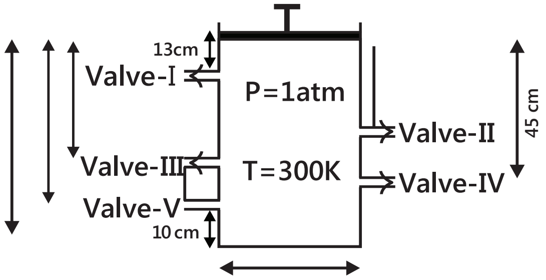
(A) 0.4 (B) 0.6 (C) 0.5 (D) 0.8

Q.7 A spherical balloon of 21 cm diameter is to be filled up with hydrogen at N.T.P. from a cylinder containing the gas at 20 atm at 27°C. If the cylinder can hold 2.82 litre of water, the number of balloon/s that can be filled up are:

(A) 5 (B) 10 (C) 20 (D) None of these

Q.8 A container fitted with frictionless massless piston consist of five valves-I, II, III, IV and V. These valves open automatically if pressure exceed over 1.5, 2.2, 2.5, 4.4 and 4.8 atm respectively. Under the given initial conditions (mentioned in given diagram) system is in state of equilibrium Piston is now pressed in downward direction very slowly.

[**Note:** Consider the diameter of value tube negligible and temperature remain constant.]



Select the correct option(s).

(A) Value-II will be opened first

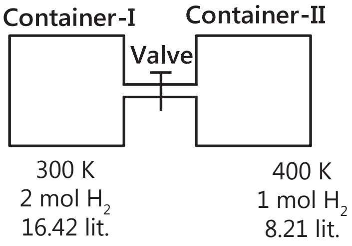
(B) As the piston crosses the valve which will be opened first, the remaining number of moles in container are $\frac{5}{3}$.

(C) Valve-V will be the second valve which is open

(D) Number of moles will zero as piston crosses Valve-V

Multiple Correct Choice Type

Q.9 Select the correct option(s):



(A) Pressure in container-I is 3 atm before opening the valve

(B) Pressure after opening the valve is 3.57 atm.

(C) Moles in each compartment are same after opening the valve

(D) Pressure in each compartment are same after opening the valve

Q.10 Select the correct observation for a 8.21 lit container, filled with 2 moles of He at 300 K,

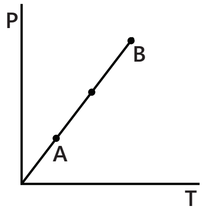
(A) It has pressure 6 atm

(B) If it is an open rigid container, its pressure increases to 8 atm on heating to 400 K

(C) If it is closed non-rigid (like thin skin balloon), its volume increases to 16.42 lit. on heating to 600 K

(D) When connected with another similar empty container maintained at 150 K while maintaining original container at 300 K, pressure reduces to $\frac{2}{3}$ atm.

Q.11 Select the correct option for an ideal gas undergoing a process as shown in diagram.:



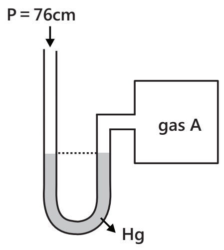
(A) If 'n' is changing, 'V' must also be changing

(B) If 'n' is constant, 'V' must be constant

(C) If 'n' is constant, 'V' must be changing

(D) If 'h' is changing. 'V' must be constant

Q.12 An open ended mercury manometer is used to measure the pressure exerted by a trapped gas as shown in the figure. Initially manometer shows no difference in mercury level in both columns as shown in diagram.



After sparking 'A' dissociates according to following reaction $2A(g) \longrightarrow 3B(g) + 2C(g)$

If pressure of Gas "A" decreases to 0.8 atm, then (Assume temperature to be constant and is 300 K)

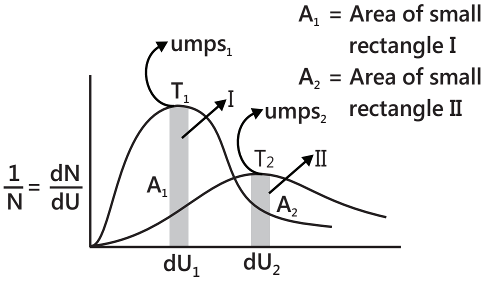
(A) Total pressure increased by 1.3 atm

(B) Total pressure increased by 0.3 atm

(C) Total pressure increased by 22.3 cm of Hg

(D) Difference in mercury level is 228 mm

Q.13 Following represents the Maxwell distribution curve for an ideal gas at two temperatures T_1 & T_2. Which of the following option(s) are true?



(A) Total area under the two curves is independent of moles of gas

(B) If du_1 = f $umps_1$ & du_2 = f $umps_2$ then $A_1 = A_2$

(C) $T_1 > T_2$ and hence higher the temperature, sharper the curve

(D) The fraction of molecules having speed = umps decreases as temperature increase

Q.14 Select the correct option(s).

(A) Fraction of molecule in the range $u_{avg} = fu_{avg}$ is same for SO_2 and O_2 at same temperature $(0 < f < 1)$.

(B) Fraction n or f molecule in the range u_{mps} = 100(m/sec) is same for SO_2 and O_2 at same temperature.

(C) Fraction of molecule in the range $u_{avg} = fu_{avg}$ is same for O_2 at 300 K and at 200 K$(0 < f < 1)$

(D) None of these

Q.15 Which of the following statements are correct?

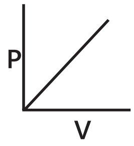
(A) Helium diffuses at a rate 8.65 times as much as CO does

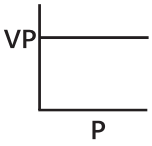
(B) Helium escapes at a rate 2.65 times as fast as CO does

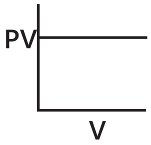
(C) Helium escapes at a rate 4 times as fast as CO_2 does

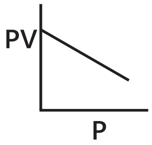
(D) Helium escapes at a rate 4 times as fast as SO_2 does

Q.16 Which of the following graphs represent Boyle's law?

(A)


(B)


(C)


(D)


Q.17 The value of the molar gas constant is:

(A) 8.3145×10^3 (kg mol)$^{-1}$ K^{-1}

(B) 1.987 cal mol K^{-1}

(C) 0.083145×10^3 dm^3 bar mol^{-1} K^{-1}

(D) 0.083145 dm^3 bar mol^{-1} K^{-1}

Q.18 When a gas is expanded at constant temperature:

(A) The pressure decreases

(B) The kinetic energy of the molecules remains the same

(C) The kinetic energy of the molecules decreases

(D) The number of molecules of the gas decrease

Q.19 Which of the following are correct statements?

(A) Vander Waal's constant 'a' is a measure of attractive force

(B) Vander Waal's constant 'b' is also called co-volume or excluded volume

(C) 'b' is expressed in L mol^{-1}

(D) 'a' is expressed in atm L^2 mol^{-2}

Assertion Reasoning Type

In each of the following questions, a statement of Assertion (A) is given followed by a corresponding statement of Reason (R) just below it. Of the statements, mark the correct answer as

(A) If both assertion and reason are true and reason is the correct explanation of assertion

(B) If both assertion and reason are true but reason is not the correct explanation of assertion.

(C) If assertion is true but reason is false.

(D) If both assertion and reason are false.

(E) If assertion is false but reason is true.

Q.20 Assertion: Excluded volume or co-volume equal to (v-nb) for nmoles.

Reason: Co- Volume depends on the effective size of gas molecules.

Q.21 Assertion: Plot of P Vs. 1/V(volume) is a straight line.

Reason: Pressure is directly proportional to volume

Q.22 Assertion: CO_2 above 31.1°C and 600 bar pressure is used to remove caffeine from coffee beans.

Reason: CO_2 is gaseous in nature.

Q.23 Assertion: Gas with lower mass will effuse or diffuse faster.

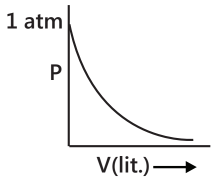
Reason: Kinetic energy of any gas depends upon its mass.

Q.24 Assertion: CH_4, CO_2 has value of Z (compressibility factor) less than one.

Reason: Z < 1 is due to repulsive forces among the molecules.

Comprehension Type

Paragraph 1: On the recently discovered 10th planet it has been found that the gases follow the relationship $Pe^{v/2} = nCT$ where C is constant other notation are as usual (V in L, P in atm and T in Kelvin). A curve is plotted between P and V at 500 K and 2 moles of gas as shown in figure



Q.25 The value of constant C is

(A) 0.01 (B) 0.001 (C) 0.005 (D) 0.002

Q.26 Find the slope of the curve plotted between P Vs T for closed container of volume 2 lit. having same moles of gas.

(A) $\frac{e}{2000}$ (B) 2000 e

(C) 500 e (D) $\frac{2}{1000\,e}$

Q.27 If a closed container of volume 200 lit. of O_2 gas (ideal gas) at 1 atm & 200 K is taken to planet. Find the pressure of oxygen gas at the planet at 821 K in same container

(A) $\frac{10}{e^{100}}$ (B) $\frac{20}{e^{50}}$ (C) 1 atm (D) 2 atm

Paragraph 2: For a gaseous reaction,

$2A(g) \longrightarrow 3B(g) + C(g)$

Whose extent of dissociation depends on temperature is performed in a closed container, it is known that extent of dissociation of A is different in different temperature range. Within a temperature range it is constant. (Temperature range $T_0 - T_1$, $T_1 - T_2$, $T_2 - T_\infty$). A plot of P v/s T is drawn under the given condition. Given: tan 55 = 1.42, tan 50 = 1.19, tan 60 = 1.73.

Q.28 If $\alpha_{T_i-T_{i+1}}$ is the degree of dissociation of A then in the temperature:

range $T_i \to T_{i+1}$

(A) $\alpha_{T_0-T_1}$ is lowest (B) $\alpha_{T_0-T_1}$ is highest

(C) $\alpha_{T_2-T_\infty} = 1$ (D) $\alpha_{T_2-T_\infty} = 0$

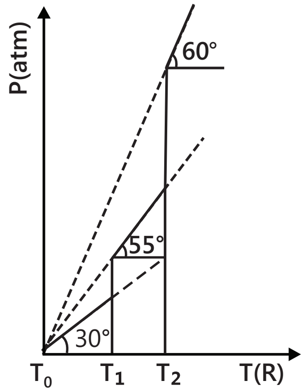
Q.29 If initially 1 mole of A is taken in a 0.0821 l container then [R = 0.0821 atm lit/k]

(A) $\alpha_{T_0-T_1} = 0.19$

(B) $\alpha_{T_0-T_1} = 0.095$

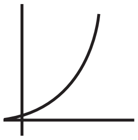
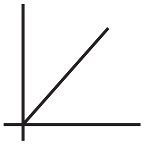
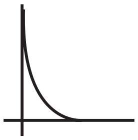
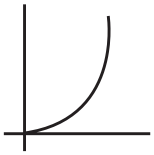
(C) $\alpha_{T_1-T_2} = 0.42$

(D) $\alpha_{T_1-T_2} = 0.73$

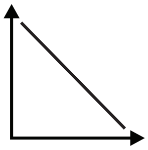
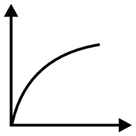
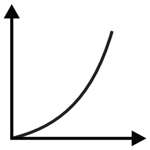
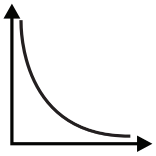


Match the Columns

Q.30 Match the description in Column I with graph provided in Column II. For n moles of ideal gas at temperature T.

Column I	Column II
(A) $\frac{P}{V}$ vs P	(p) 
(B) $\frac{P}{V}$ vs V	(q) 
(C) $\frac{V}{P}$ vs P^{-2}	(r) 
(D) $\frac{P}{V}$ vs log P	(s) 

Q.31 Match the entries in column I with entries in Column II and then pick out correct options:

Column I	Column II
(A) $\frac{1}{V^2}$ vs P for	(p)  Ideal gas at constant T and n
(B) V vs $\frac{1}{T}$ for	(q)  Ideal gas at constant P and n
(C) log P vs log V	(r)  For ideal gas at constant T and n.
(D) V vs $\frac{1}{P^2}$ for	(s)  Ideal gas at constant T and n.

Previous Years' Questions

Q.1 The ratio of root mean square velocity to average velocity of a gas molecule at a particular temperature is ***(1981)***

(A) 1.086: 1 (B) 1: 1.086

(C) 2: 1.086 (D) 1.086: 2

Q.2 Equal weights of methane and oxygen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by oxygen is ***(1981)***

(A) $\frac{1}{3}$ (B) $\frac{1}{2}$ (C) $\frac{2}{3}$ (D) $\frac{1}{3} \times \frac{273}{298}$

Q.3 Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of a helium atom is ***(1982)***

(A) Two times that of a hydrogen molecule

(B) Same as that of a hydrogen molecule

(C) Four times that of a hydrogen molecule

(D) Half that of a hydrogen molecule

Q.4 The value of van der Waals' constant 'a' for the gases O_2, N_2, NH_3 and CH_4 are 1.360, 4.170 and 2.253 L_2 atm mol^{-2} respectively. The gas which can most easily be liquefied is ***(1989)***

(A) O_2 (B) N_2 (C) NH_3 (D) CH_4

Q.5 A gas will approach ideal behaviour at **(1999)**

(A) Low temperature and low pressure

(B) Low temperature and high pressure

(C) High temperature and low pressure

(D) High temperature and high pressure

Q.6 The rms velocity of hydrogen is $\sqrt{7}$ times the rms velocity of nitrogen. If T is the temperature of the gas ***(2000)***

(A) $T(H_2) = T(N_2)$ (B) $T(H_2) > T(N_2)$

(C) $T(H_2) < T(N_2)$ (D) $T(H_2) = \sqrt{7}\ T(N_2)$

Q.7 At 100°C and 1 atm if the density of the liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3} then the volume occupied by water molecules in 1 L of steam at this temperature is ***(2000)***

(A) 0.040 cm^3 (B) 0.065 cm^3

(C) 0.060 cm^3 (D) 0.045 cm^3

Q.8 The term that corrects for the attractive forces present in a real gas in the van der Waals' equation is ***(2009)***

(A) nb (B) n^2a/V^2

(C) $-(n^2a/V^2)$ (D) – nb

Q.9 If a gas is expanded at constant temperature ***(1986)***

(A) The pressure decreases

(B) The kinetic energy of the molecules remains the same

(C) The kinetic energy of the molecules decreases

(D) The number of molecules of the gas increases

Q.10 As gas described by van der Waals' equation ***(2008)***

(A) Behaves similar to an ideal gas in the limit of large molar volumes

(B) Behaves similar to an ideal gas in the limit of large pressures

(C) Is characterized by van der Waals' coefficients that are dependent on the identity of the gas but are independent of the temperature.

(D) Has the pressure that is lower than the pressure exerted by the same gas behaving ideally

Q.11 According to kinetic theory of gases ***(2011)***

(A) Collisions are always elastic

(B) Heavier molecules transfer more momentum to the well of the container

(C) Only a small number of molecules have very high velocity

(D) Between collisions, the molecules move in straight lines with constant velocities

Read the following question and answer as per the direction given below:

(a) Statement-I is true: statement-II is true: statement-II is the correct explanation of statement I.

(b) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement I.

(c) Statement-I is true; statement-II is false.

(D) Statement-I is false; statement-II is true.

Q.12 Statement-I: The value of van Waals' constant 'a' is larger for ammonia than for nitrogen.

Statement-II: Hydrogen bonding is present in ammonia. ***(1998)***

Q.13 Statement-I: The pressure of a fixed amount of an ideal gas is proportional to its temperature.

Statement-II: Frequency of collisions and their impact both increase in proportion to the square root of temperature. ***(2000)***

Q.14 Match the gases under specified conditions listed in Column I with their properties/laws in Column II. ***(2007)***

Column I	**Column II**
(A) Hydrogen gas (p = 200 atm, T = 273 k)	(p) Compressibility factor ≠ 1
(B) Hydrogen gas (p ~ 0, T = 273 K)	(q) Attractive foresees are dominant
(C) CO_2 (p = 1 atm, T = 273 K)	(r) pV = nRT
(D) Real gas with very large molar volume	(s) P(V – nb) = nRT

Q.15 To an evacuated vessel with movable piston under external pressure of 1 atm, 0.1 mole of He and 1.0 mole of an unknown compound (vapour pressure 0.68 atm 0ºC) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0ºC is close to ***(2011)***

Q.16 A mixture of ethane (C_2H_6) and ethene (C_2H_4) occupies 40 L at 1.00 atm and at 400 K. The mixture reacts completely with 130 g of O_2 to produce CO_2 and H_2O Assuming ideal gas behaviour, calculate the mole fractions of C_2H_4 and C_2H_6 in the mixture.

Q.17 The compression factor (compressibility factor) for one mole of a van der Waals' gas at 0ºC and 100 atm pressure is found to be 0.5 Assuming that the volume of a gas molecule is negligible, calculate the van der Waals' constant 'a'. ***(2001)***

Q.18 At 400 K, the root mean square (rms) speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of the gas Y is ***(2009)***

Q.19 Match gases under specified conditions listed in Column I with their properties/laws in Column II. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS. ***(2007)***

Column I	**Column II**
(A) Hydrogen gas (P = 200 atm, T = 273K)	(p) Compressibility factor ≠ 1
(B) Hydrogen gas (P ~ 0, T = 273K)	(q) Attractive forces are dominant
(C) CO_2 (P = 1 atm, T = 273K)	(r) PV = nRT
(D) Real gas with very large molar volume	(s) P(V − nb) = nRT

Q.20 A gas described by van der Waal's equation ***(2008)***

(A) behaves similar to an ideal gas in the limit of large molar volumes

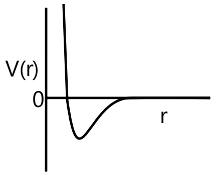
(B) behaves similar to an ideal gas in the limit of large pressures

(C) is characterized by van der Waal's coefficients that are dependent on the identity of the gas but are independent of the temperature

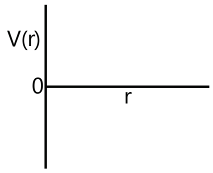
(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally

Q.21 One mole of a monoatomic real gas satisfies the equation p(V – b) = RT where b is a constant. The relationship of interatomic potential V(r) and interatomic distance r for the gas is given by ***(2015)***

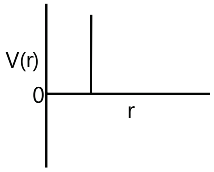
(A)



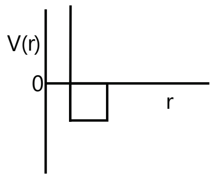
(B)



(C)



(D)



Q.20 The diffusion coefficient of an ideal gas is proportional to its mean free path and mean speed. The absolute temperature of an ideal gas is increased 4 times and its pressure is increased 2 times. As a result, the diffusion coefficient of this gas increases x times. The value of x is ***(2015)***

Questions

JEE Main/Boards

Exercise 1

Q.4 Q.6 Q.11
Q.16 Q.20 Q.21
Q.26

Exercise 2

Q.3 Q.5 Q.10
Q.12 Q.28

Previous Years' Questions

Q.1 Q.6 Q.10

JEE Advanced/Boards

Exercise 1

Q.5 Q.7 Q.11
Q.16 Q.20 Q.26
Q.30

Exercise 2

Q.6 Q.8 Q.11
Q.21

Previous Years' Questions

Q.5 Q.6 Q. 14
Q.16

Answer Key

JEE Main/Boards

Exercise 1

Q.1 1870.65J

Q.2 41.33 g

Q.3 3.42 g per litre

Q.4 Volume of the gas will remain constant

Q.5 89.65 L

Q.6 S_8

Q.7 $1:\sqrt{24}$

Q.8 5.24 Litres

Q.9 $\sqrt{8}:1$

Q.10 0.137

Q.11 14.14 dm^3

Q.12 390 m sec^{-1}

Q.13 2.7×10^{10}

Q.14 0.856 litres

Q.15 1.0043

Q.16 –173°C, 0.82 litre

Q.17 0.787 atoms

Q.18 750 K

Q.19 1: 3

Q.20 2.197 atmosphere

Q.21 7.09×10^6 g

Q.22 $P_A: P_B$ is 8: 1

Q.23 83.75 cm of Hg

Q.24 3 cm

Q.25 a = 6.52 atm L^2 $mole^{-1}$

Q.26 123. 15

Q.27 0.492 atm 0.246 atm

Exercise 2

Single Correct Chioce Type

Q.1 B **Q.2** A **Q.3** C **Q.4** B **Q.5** B **Q.6** B

Q.7 C **Q.8** D **Q.9** C **Q.10** D **Q.11** B **Q.12** B

Q.13 B **Q.14** A **Q.15** A **Q.16** A **Q.17** C **Q.18** B

Q.19 B

Previous Years' Questions

Q.1 A **Q.2** C **Q.3** A **Q.4** B **Q.5** C **Q.6** A

Q.7 A **Q.8** C **Q.9** B **Q.10** C **Q.11** B **Q.12** A

Q.13 D **Q.14** A **Q.15** A **Q.16** C **Q.17** C **Q.18** B

Q.19 B

JEE Advanced/Boards

Exercise 1

Q.1 71.4 L

Q.2 P = 0.062 atm, T = 75 K

Q.3 16.07 gm; 12 dm^3

Q.4 1/4

Q.5 25%

Q.6 $P_{total} = 27.54 \times 10^5\ N/m^2$,

$P_{final} = 19.66 \times 10^5\ N/m^2$

Q.7 (i) $\frac{2}{1}$; (ii) $\frac{3}{16}$; (iii) 2: 1

Q.8 4.46

Q.9 2

Q.10 Yes

Q.11 183,800 cm/sec

Q.12 8.68×10^5 (cm/s) ; 71.27 K

Q.13 u_{rms} = 493m/s, u_{ms} = 403m/s, u_{av} = 454.4 m/s

Q.14 8.303×10^{-3}

Q.15 0.199

Q.16 (i) 0.012 atm; (ii) 2.5×10^{22}; (iii) 3.05 J; (iv) 258; (v) $\frac{1}{\sqrt{2}}$; (vi) 0.4×10^{-3}: 1

Q.17 He

Q.18 (a) 5.306×10^2 Pa, (b) 1.281×10^{21} mol/vol

Q.19 (i) P_1 = 5 atm; (ii) T_3 = 360 K; (iii) V_1 = 16 lit; (iv) P_2 = 1.5 atm ; (v) T_4 = 90 K

Q.20 $P \propto d$; $p = kd$ & $k = \frac{1\text{atm}}{1\text{meter}}$; (a) 80; (b) 1295 moles

Q.21 6 atm, No

Q.22 314 pm, 7.051 cm,6742 s^{-1}, $1.08 \times 10^{17} cm^{-3} s^{-1}$

Q.23 $n = \frac{-T}{100} + 5$, $V = \frac{-RT^2}{100} + 5RT$, $V_{max} = 51.3125$

Q.24 2 atm

Q.25 421.9 K

Q.26 2.2 g

Q.27 (a) 0.625, (b) 4

Q.28 10 Step, 27.78 mol CH_4, 5333.3 mol O_2

Q.29 4: 7: 5

Q.30 (a) Bulb A: $N_2(g)$, $CO_2(g)$; Bulb B: $N_2(g)$, $H_2O(s)$

(b) No. of mole of $H_2(g)$ = 0.0025; (c) Bulb A: $N_2(g)$; Bulb B: $N_2(g)$, $H_2O(s)$; Bulb C: $N_2(g)$, $CO_2(s)$

Exercise 2

Single Correct Chioce Type

Q.1 C **Q.2** B **Q.3** C **Q.4** C **Q.5** C **Q.6** B **Q.7** B
Q.8 C

Multiple Correct Chioce Type

Q.9 B, D **Q.10** A, D **Q.11** A, B **Q.12** B, D **Q.13** A, B, D **Q.14** A, C **Q.15** B, C
Q.16 B, C **Q.17** B, D **Q.18** A, B **Q. 19** A, B, C, D

Assertion Reasoning Type

Q.20 E **Q.21** D **Q.22** A **Q.23** C **Q.24** A

Comprehension Type

Paragraph 1: **Q.25** B **Q.26** D **Q.27** A

Paragraph 2: **Q.28** A **Q.29** C

Match the Columns

Q.30 A → s; B → r; C → q; D → p **Q.31** A → r; B → s; C → p; D → q

Previous Years' Questions

Q.1 A **Q.2** A **Q.3** B **Q.4** C **Q.5** C **Q.6** C **Q.7** C

Q.8 B **Q.9** A, B **Q.10** A, C **Q.11** A, C, D **Q.12** A **Q.13** D

Q.14 A → p, s; B → r; C → p,q; D → r **Q.15** 7 **Q.16** 0.34 **Q.17** $a = 1.25$ atm L^2 mol^{-2}

Q.18 D **Q.19** A → p, s; B → r; C → p, q; D → p, s **Q.20** A, C, D **Q.21** C **Q.22** D

Solutions

JEE Main/Boards

Exercise 1

Sol 1: T = 27°C = 300 K

Mass of CH_4 (per mole) = 16 g

Mass of CH_4 (given) = 8 g

$\Rightarrow n = \text{number of moles} = \frac{8}{16} = 0.5$

K.E. (per mole) = $\frac{3}{2}$ RT

K.E. (Total) = $\frac{3}{2}$ RT × n

$= \frac{3}{2} \times 8.314 \times 300 \times 0.5 = 1870.65$ J

Sol 2: Let molecular weight of gas be 'M' grams

$\Rightarrow$ moles of gas (at 25°C) = $\frac{3.7}{M}$

PV = nRT

$\Rightarrow P_1V_1 = \frac{3.7}{M} R \times 298$

For hydrogen,

n (given) = $\frac{0.184}{2} = \frac{0.184}{2}$

T = (17 + 273) = 290 K

$P_2V_2 = \frac{0.184}{2} R \times 290$

As pressure and volumes are same,

$P_1V_1 = P_2V_2$

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

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

Sol 3: T = 30°C = 303 K

P = 5 atm

R = 0.0821 lit atm / (mol k)

$M_{(NH_3)} = 17 \text{ g} = 17 \times 10^{-3}$ kg

Using PM = ρRT

$5 \times 17 \times 10^{-3} = \rho \times 0.0821 \times 303$

$\Rightarrow \rho = 3.42 \times 10^{-3}$ kg/litre = 3.42 g/l

Sol 4: Volume will remain constant because volume of container cannot be increased or decreased. Hence mole of N_2 will decrease with decrease in pressure.

Sol 5: Moles of $H_2 = \frac{6}{2} = 3$ moles

P = 1.5 atm

T = 273 + 273 = 546 K

Using PV = nRT

1.5V = 0.0821 × 3 × 546

V = 89.65 litres

Sol 6: Moles of sulphur = $\frac{3.2}{32} = 0.1$

$nS \rightarrow S_n$

1 atm = 760 mm of Hg

Pressure = $\frac{723}{760}$ atm = 0.95 atm

Volume = 780 mL = 0.78 ℓ

T = 450°C = 723 K

PV = nRT

$\Rightarrow n = \frac{0.95 \times 0.78}{0.0821 \times 723}$

N = 0.012

$\Rightarrow 0.1 = 0.012 \times n$ [Sulphur mass balance]

$\Rightarrow n = \frac{0.1}{0.012} = 8$

Sol 7: Given

$\frac{r_A}{r_B} = \frac{1}{4}$ and $\frac{M_A}{M_B} = \frac{W_A}{W_B} = \frac{2}{3}$

According to Graham's law of diffusion

$r_A \propto \frac{P}{\sqrt{M}}$; $P = \frac{nRT}{V}$

$$\frac{r_A}{r_B} = \frac{n_A\sqrt{M_B}}{n_B\sqrt{M_A}}$$

$$\frac{1}{4} = \sqrt{\frac{M_B n_A^2}{M_A n_B^2}}$$

$$\Rightarrow \frac{n_B^2 M_A}{n_A^2 M_B} = \frac{16}{1}$$

$$\frac{n_A M_A}{n_B M_B} = \frac{2}{3} \Rightarrow \frac{M_A}{M_B} = \frac{2}{3}\frac{n_B}{n_A}$$

$$\frac{n_B^3}{n_A^3}\frac{2}{3} = 16$$

$$\Rightarrow \left(\frac{n_B}{n_A}\right)^3 = 24$$

$n_A : n_B = 1 : \sqrt{24}$

Ratio of mole fractions = ratio of moles

Sol 8: Acetylene = C_2H_2 H–C≡C–H

(n) moles of acetylene = $\frac{5}{26}$

T = 50ºC = 313 K

P = 740 mm of Hg = $\frac{740}{760}$ atm

PV = nRT

$$\frac{740}{760} \times V = \frac{5}{26} \times 0.0821 \times 323$$

$\Rightarrow$ v = 5.24 litres

Sol 9: P = 20 bar

$$\frac{r_{He}}{r_{CH_4}} = \frac{n_{He}}{n_{CH_4}}\sqrt{\frac{M_{CH_4}}{M_{He}}} = \sqrt{\frac{16}{2}} = \sqrt{\frac{8}{1}}$$

$= \sqrt{8} : 1$

Sol 10: $Cl_2 \xrightarrow{\quad} 2Cl$

$1 - x \qquad 2x$

T = 1200 ºC = 1473 K

Given $\frac{r_{Kr}}{r_{mix}} = \frac{1}{1.16}$

$$\frac{r_{Kr}}{r_{mix}} = \sqrt{\frac{M_{mix}}{M_{Kr}}} \Rightarrow \frac{M_{mix}}{84} = \frac{1}{(1.16)^2}$$

$$\Rightarrow M_{mix} = \frac{84}{(1.16)^2}$$

$M_{mix} = 62.425$

We know

$$62.425 = \frac{(1-x)\times 71 + 2x \times 35.5}{1+x}$$

$$62.425 = \frac{71}{1+x}$$

$$\Rightarrow 1 + x = \frac{71}{62.425}$$

$$\therefore x = \frac{71 - 62.425}{62.425} = 0.137$$

Sol 11: V = 20 dm^3 = 20 × 10^{-3} m^3 = 20 litre

T = 60 sec

We know

Rate of diffusion $\propto \frac{1}{\sqrt{\text{Molecular weight}}}$

$$\Rightarrow \frac{r_{SO_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{SO_2}}}$$

$$\frac{V_{SO_2}/60}{V_{O_2}/30} = \sqrt{\frac{32}{64}}$$

$$\Rightarrow \frac{20\times 30}{60\times V_{O_2}} = \sqrt{\frac{1}{2}}$$

$$\Rightarrow V_{O_2} = 10\sqrt{2}$$

$$V_{O_2} = \sqrt{200}$$

V_{O_2} = 14.14 dm^3

Sol 12: T = 20 ºC = 293 K; P = 82 cm of Hg

$\Rightarrow$ P = $\frac{82}{76}$ = 1.08 atm = 1.09 × 10^5 Pa

$O_3 \Rightarrow$ Molecular weight = 48 × 10^{-3} g

Root mean square velocity

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

$$V = \sqrt{\frac{3\times 8.314\times 293}{48\times 10^{-3}}}$$

V = 390 m/s

Sol 13: $P = 7.6 \times 10^{-10}$ mm pf Hg

V = 1 litre

T = 0 °C = 273 K

Number of molecules = Moles × N_A

$PV = nRT$; $\frac{7.6\times 10^{-10}}{760} \times 1 = n \times 0.0821 \times 273$

$$\Rightarrow \ n = \frac{10^{-12}}{0.0821\times 273}$$

Number of molecules = $\frac{6.023\times 10^{23}\times 10^{-12}}{0.0821\times 273}$

= 2.7×10^{10} molecules

Sol 14: T = 27 °C = 300 K

P = 2 atm

P(solid CO_2) = 1.53 g/mℓ

V_{occupied} = 2mℓ

⇒ M (Solid CO_2) = p × v

= 1.53 × 2 g = 3.06 g

⇒ Moles of solid CO_2

$$= \frac{3.06}{44} = 0.07$$

Using PV = nRT (for gaseous CO_2) ;

2 × V = 300 × 0.07 × 0.0821

V = 0.86 litre

Sol 15: M ($^{336}UF_6$) = 235 + 18 × 6 = 343

M ($^{238}UF_6$) = 238 + 18 × 6 = 346

$$r^2 \propto \frac{1}{M}$$

$$\frac{r^{235}UF_6}{r^{238}UF_6} = \sqrt{\frac{346}{343}}$$

Sol 16: Let molecular weight = M = 120 g

$$\Rightarrow \text{Moles of gas} = \frac{12}{M} = \frac{12}{120} = 0.1 \text{ moles}$$

$P_1 = P$

$P_2 = 1.1\,P$

T_1 = T°C = T + 273 K

T_2 = (T + 10) °C = T + 283 K

P_1 = 1 atm

Using $P \propto T$

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

$$\frac{P}{1.1P} = \frac{T+273}{T+283}$$

T + 283 = 1.1 t + 273 × 1.1

$$\Rightarrow t = \frac{283 - 1.1\times 273}{0.1}$$

T = – 173 °C

1 × V = 0.0821 × 0.1 × (– 173 + 273)

⇒ V = 0.0821 × 0.1 × 100

V = 0.821 litre

Sol 17: $\frac{n_{H_2}}{n_{O_2}} = 2:1$

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Total pressure (before reaction) = 0.8 atm

T = 20 °C = 293 K

Let total moles in container be

∴ 3 (2 moles of H_2 and 1 mole O_2)

After the reaction (180% complete)

Moles of H_2 = 2 – 2 × 0.8 = 0.4

Moles of O_2 = 1 – 1 × 0.8 = 0.2

Moles of H_2O = 0.8 × 2 = 1.6

⇒ Total moles after reaction

= 1.6 × 0.2 + 0.4 = 2.2 mole

Using PV = nRT

and same volume, we get

$$\frac{P_1}{n_1 t_1} = \frac{P_2}{n_2 t_2}$$

$$\frac{0.8}{3\times 293} = \frac{P_2}{2.2\times 393}$$

⇒ P_2 = 0.787 atm

Sol 18: Vessel is open ⇒ $P_1 = P_2$ = atm and volume is constant

$\therefore n_1T_1 = n_2T_2$

$n \times 300 = \left(1 - \frac{3}{5}\right) n \times T$

$T_2 = \frac{300 \times 5}{2}$

$T_2 = 750$ K

Sol 19: Let molecular weight of a and B be M_A and M_B respectively

$\Rightarrow n_A = \frac{2}{M_A}$

$n_B = \frac{3}{M_B}$

Given $1 \times V = n_A \times R \times T$

$1.5 \times V = n_A + n_B \times R \times T$

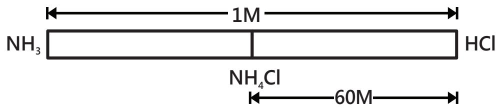
$\Rightarrow \frac{1}{1.5} = \frac{n_A}{n_A + n_B}$

$\Rightarrow \frac{n_A}{n_B} = 2$

$\Rightarrow \frac{2N_B}{M_A \times 3} = 2$

$\Rightarrow M_B / M_A = 3 : 1$

Sol 20:



We know

$r \propto \frac{P}{\sqrt{M}}$

$\frac{r_{NH_3}}{r_{HCl}} = \frac{1}{P} \times \sqrt{\frac{N_{HCl}}{M_{NH_3}}}$

$\frac{d_{NH_3}/t}{d_{HCl}/t} = \frac{1}{P} \times \sqrt{\frac{36.5}{17}}$

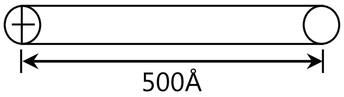
$\frac{d_{NH_3}}{d_{HCl}} = \frac{1}{P} \times 1.465$

$\frac{40}{60} = \frac{1.465}{P}$

$\Rightarrow P = 2.197$ atm

Sol 21:

d = 150Å



Volume of particle

$= \pi r^2 l = \frac{\pi d^2 L}{4} = \frac{3.14 \times (150)^2 \times 500 \times 10^{-30}}{4}$

$= 8.836 \times 10^{-24}\ m^3$

Specific volume = 0.75 cm^3 / g

Mass of virus = $\frac{\text{Volume}}{\text{Specific value}}$

$= \frac{8.836 \times 10^{-24} m^3}{0.75 \times 10^{-6} m^3 / g} = 1.178 \times 10^{-17}$ g

Molecular weight = mass × NA = 7.09×10^6 g

Sol 22: Gives mA = 2mB

r.m.s. (A) = 2 r.m.s.(B)

Both contain same no. of molecules ⇒ V is same

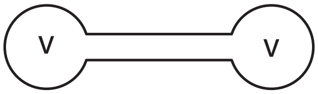
$\text{r.m.s.} \propto \sqrt{\frac{P}{M}}$

$\frac{\text{r.m.s.A}}{\text{r.m.s.B}} = \sqrt{\frac{P_A \times M_B}{M_A \times P_B}}$

$2 = \sqrt{\frac{P_A}{2P_B}}$

$\Rightarrow \frac{P_A}{P_B} = 8:1$

Sol 23:



$T_1 = 0°C$

Let initially there be n-moles in both the bulbs.

When bulbs-2 is placed in water both the pressure in both bulbs must be same

$\Rightarrow n_1 \times R \times (62 + 273) = n_{II} \times R \times 273$

$$\Rightarrow \frac{n_I}{n_{II}} = \frac{273}{335}$$

and $n_I + n_{II} = n$

$$\Rightarrow n_{II} + \frac{273}{335} n_{II} = n$$

$$\Rightarrow n_{II} = \frac{335n}{608}$$

$$\Rightarrow n_I = \frac{273n}{608}$$

Pressure in bulbs

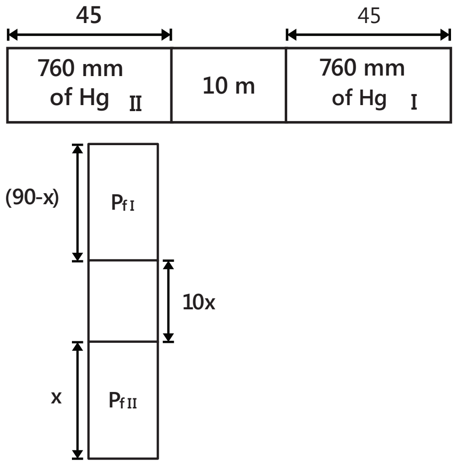
$$P_1 \times V_1 = \frac{n}{2} \times R\ (273)$$

$$P_2 \times V_2 = \frac{273n}{608} \times R \times (273 + 62)$$

$$\Rightarrow \frac{P_2}{P_1} = \frac{335 \times 273 \times 2}{608 \times 273}$$

$$P_2 = \frac{335 \times 2}{608} \times P_1 = 1.10\ P_1 = 83.75 \text{ cm of Hg}$$

Sol 24:



Applying P and P-V balance

for compartment-I

$760 \times 45 = P_{fI} \times (90 - x)$

For compartment-II

$760 \times 45 = (P_{fI} + 10) \times x$

$$\Rightarrow P_{fI} = \frac{760 \times 45}{90 - x}$$

$$P_{fI} = \frac{760 \times 45}{x} - 100$$

$$\Rightarrow \frac{760 \times 45}{90 - x} = \frac{760 \times 45}{x} - 100$$

$\Rightarrow 3420\ x = (3420 - 10x)\ (90 - x)$

$3420\ x = 3420 \times 90 - 900x +$

$10x^2 - 3420x$

$10x^2 - 7740\ x + 3420 \times 90 = 0$

$\Rightarrow x^2 - 774\ x + 30780 = 0$

$$x = \frac{774 \pm \sqrt{774^2 - 4 \times 30780}}{2}$$

$\Rightarrow x = 42$ cm

$\therefore$ In the vertical column the mercury column has shifted by 3 cm

Sol 25: P = 11 V; V = 4 litre

T = 300 K ; n = 2

b = 0.05 litre / n

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

$$\left(11 + \frac{a \times 4}{16}\right) . (4 - 2 \times 0.05) = 2 \times 0.0821 \times 300$$

$$\left(11 + \frac{a}{4}\right) (4 - 0.1) = 49.26$$

$$\left(11 + \frac{a}{4}\right) = 12.62$$

a = 6.492

Sol 26: Mass of liquid = 148 – 50 = 48 g

Density = 0.98 g/mL

$$\text{Volume} = \frac{98}{0.98} \text{ mL} = 100 \text{ mL} = 0.1\ \ell$$

Mass of gas = 50.5 – 50 = 0.5 g

P = 760 mm of Hg = 1 atm

T = 300 K ; PV = nRT

$$1 \times 0.1 = \frac{0.5}{M} \times 0.0821 \times 300$$

$\Rightarrow M = 5 \times 300 \times 0.0821$

M = 123.15 g

Sol 27: V = 10 litre

T = 27 ºC

n(He) = $\frac{0.4}{4}$ g = 0.1 mole

$\Rightarrow P_{He} \times 10 = 300 \times 0.0821 \times 0.2$

$P_{He} = 0.2464$

$n_{O_2} = \frac{1.6}{32} = 0.05$

$P_{O_2} \times 10 = 0.05 \times 0.0821 \times 300$

$P_{O_2} = 0.123$

$n_{N_2} = \frac{1.4}{28} = 0.05$

$\Rightarrow P_{N_2} \times 10 = 0.05 \times 0.082 \times 300 = 0.123$

$P_{total} = P_{O_2} + P_{N_2} + P_{He}$

$= 0.123 + 0.123 + 0.246 = 0.492$

Exercise 2

Single Correct Choice Type

Sol 1: (B) V = 0.16 ℓ

AIM $\xrightarrow{\quad}$ to find slope of P–T curve

PV = nRT

$\frac{P}{T} = \frac{nR}{V}$

$2Ag(g) \xrightarrow{\quad} 3\,B(g) \quad + \quad 2C(g)$

1–0.4	$\frac{3}{2}(0.4)$	$\frac{2}{2} \times 0.4$
0.6	0.6	0.4

Total moles $\xrightarrow{\quad}$ 0.6 + 0.6 + 0.4

$\xrightarrow{\quad}$ 1.6

Slope $\tan\theta = \frac{P}{T} = \frac{nR}{V} = \frac{1.6 \times 0.08}{0.16}$

$\tan\theta = 0.8$

$\theta = \tan^{-1} 0.8$

Sol 2: (A) $r_{O_2} \propto \frac{P_{O_2}}{\sqrt{M_{O_2}}} \propto \frac{n_{O_2}}{\sqrt{M_{O_2}}}$

$r_{H_2} \propto \frac{P_{H_2}}{\sqrt{M_{H_2}}} \propto \frac{n_{H_2}}{\sqrt{M_{H_2}}}$

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}\,\frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{2}{32}}\left(\frac{{}^{16}/_{32}}{{}^{2}/_{3}}\right) = \frac{1}{8}$$

Sol 3: (C) Kinetic energy of CO_2 at T K

Total K.E. of energy $\xrightarrow{\quad} \frac{3}{2}$ RT

Sol 4: (B) K.E. = $\frac{3}{2}$ RT

So at T = 300

K.E. = E = $\frac{3}{2}$ R(300)

At T = 1500

K.E. = $\frac{3}{2}$ R(1500) = $\left(\frac{3}{2}R(300)\right)$ (5) = E5 = 5E

Answer = B

Sol 5: (B) RMS velocity = $\sqrt{\frac{3RT}{M}}$

Let temperature be to

$RMS_{O_2} = RMS_{SO_2}$

$$\Rightarrow \sqrt{\frac{3RT_0}{MO_2}} = \sqrt{\frac{3RT(300)}{M_{SO_2}}}$$

$\Rightarrow T_0 = \frac{300 \times 32}{64} = 150\text{ K} \quad = -123^{\circ}\text{C}$

Sol 6: (B) $\sqrt{\frac{2RT_0}{M_{O_2}}} = \sqrt{\frac{3RT}{M_{N_2}}} = \frac{2 \times T_0}{32} = \frac{3 \times 700\text{K}}{28}$

$\Rightarrow T_0 = 1200$ K

Sol 7: (C) Final pressure, temperature = P_i, T_i

Initial pressure, temperature = P_0, T_i

Mole ratio = Mass ratio

$$= \frac{n_i}{n_0} = \frac{\frac{P_iV_i}{T_i}}{\frac{P_0V_0}{T_0}} = \frac{m_i}{m_0} = \frac{\frac{\frac{1}{2}P_0(V_0)}{\frac{2}{3}T_0}}{\frac{P_0V_0}{T_0}} = \frac{m_i}{m_0} = \frac{3}{4}$$

$\therefore$ Escaped gas = 10 – 10 × $\frac{3}{4}$ = 2.5 gms

Sol 8: (D) $P_0V_0 = nRT_0$ .....(i)

When pressure and temperature doubled

$P_iV_i = nRT_i$

$2P_0V_i = nR(2T_0)$

$V_i = \frac{nRT_0}{P_0} = V_0$ from (i)

$\therefore$ Volume remains same

Sol 9: (C) $P_0V_0 = nRT_0$ .....(i)

$P_iV_i = n_iRT_i$

Now $T_i = T_0$, $n_i = 2\ n_0$, $V_i = 2V_0$

$\therefore\ P_i = \frac{n_0RT_0}{V_0} = P_0$

$P_i = P_0 = 1$ atm

Sol 10: (D) At very low pressure, attractive forces are low, volume occupied is higher compared to volume occupied by molecule

$\Rightarrow V >> b$

$\Rightarrow$ Real gas equation

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

Sol 11: (B) y_i mole fraction of $N_2 = \frac{0.3}{0.3+0.2+0.5} = 0.3$

$\Rightarrow$ Partial pressure $= y_iP$

$= 0.3$ P atm

$= 0.3$ P × 760 mm of Hg

Sol 12: (B) 10 g each of SO_2, PH_3 and H_2 are kept in 3 flasks

We know,

Number of atom $\propto$ Number of molecule

And, for a given mass of gas

Number of mole $= \frac{\text{Mass}}{\text{Molecule weight}}$

Which implies

$\Rightarrow$ Number of molecules $\propto$ Number of moles $\propto \frac{1}{\text{Molecular weight}}$

As molecular weight of H_2 < Molecular weight PH_3 < molecular weight of SO_2

Hence, Number of molecules is in the order

$H_2 > PH_3 > SO_2$

Sol 13: (B) $P_{real} < P_{ideal}$

Due to intermolecular forces of attraction, which reduce the velocity. Hence, momentum impact on collision with wall.

Sol 14: (A) Order of Vander waal constant

A = 5.6, B = 3.6, C = 2.4

$\Rightarrow A > B > C$

Higher the Vander waal constant, higher are the attractive forces between molecules of gases and due to high attraction, liquefaction becomes easier.

Hence, ease of liquefaction has order

$A > B > C$

Sol 15: (A) Moles of $H_2 = \frac{6}{2} = 3$

P = 1.5 atm; T = 273°C = 546 K

$$V = \frac{nRT}{P} = \frac{3 \times 0.0821 \times 546}{1.5}$$

V = 89.65 mL

Sol 16: (A) $P_{max} = 14.9$ atm

$P_1 = 12$ atm, $T_1 = 27°C = 300$ K

At exploding temp $P = P_{max}$

Using $P \propto T$

$\frac{P_1}{P_2} = \frac{T_1}{T_2}$ $\Rightarrow T_2 = \frac{300 \times 14.9}{12}$

$\Rightarrow T_2 = 372$ K

Sol 17: (C) Moles of A $= \frac{2}{M_A}$

Moles of B $= \frac{3}{M_A}$

As we know volume and R are same

$$\Rightarrow \frac{P_1}{n_1T_1} = \frac{P_2}{n_2T_2}$$

$$\frac{1}{\frac{2}{M_A} \times 298} = \frac{1.5}{\left(\frac{2}{M_A} + \frac{3}{M_B}\right) \times 298}$$

$$\frac{2}{M_A}+\frac{3}{M_A}=\frac{1.5\times 2}{M_A}$$

$$\Rightarrow \frac{3}{M_A}=\frac{1}{M_A}$$

$$\frac{M_A}{M_B} = 1:3$$

Sol 18: (B) We know volume and temperature are same

$\Rightarrow P \propto n$

$$\frac{P_1}{P_2}=\frac{n_1}{n_2}\ ; \qquad \frac{P_1}{1}=\frac{44\times M_{CO_2}}{M_{H_2}\times 44}$$

$$P_1 = \frac{44}{2} = 22$$

Sol 19: (B) For ideal gas

Most probable speed = $\sqrt{\frac{3RT}{M}}$

$\therefore$ Statement A is correct and statement D is incorrect

The equation for fraction of molecule, moving with a speed at any time (equation) required

$$\frac{dN}{N}=\left(\frac{M}{2\pi RT}\right)^{1/2} e^{\frac{-mv^2}{2RT}}\,dv$$

Under similar condition of P, V and T, μ is same, hence fraction of molecules moving with $\mu_{m.p.s.}$ is

frac $\propto$ M

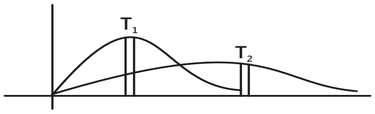
Hence, Fraction Cl_2 > frac H_2

Fraction of molecules moving with mps increases with increases in temperature

$$\mu_{\text{most probal}} \propto \frac{1}{\sqrt{M}}$$

$\therefore\ \mu_{H_2} > \mu_{Cl}$

$T_1 > T_2$



Previous Years' Questions

Sol 1: (A) $P_1V_1 = RT$

$$P_2(V_1+dV) = R(T+1)$$

$$\therefore P_2 = RT + R$$

$$\text{Since } \left(\frac{P_2}{V_1+dV}=1\right)$$

$$= 2\left(\frac{dP_2}{dT}\right)v = R$$

$$= \left(\frac{dP_2}{dT}\right) = \frac{R}{2}$$

$$\text{Since } C = Cv + \left(\frac{dP}{dT}\right)$$

$$= \frac{3R}{2}+\frac{R}{2}$$

$$= 2R$$

Sol 2: (C) PV = nRT $\therefore\ \frac{n}{V}=\frac{P}{RT}$

Sol 3: (A) In isolated system, the expansion of gas is carried out adiabatically. Since heat exchange between system and surrounding is not possible i.e., q = 0 and secondary wm is always greater than wm. Therefore, for reversible process, there must be comparatively higher decrease in intemal energy i.e., ΔU for reversible process will be more negative. Hence final temperature in reversible process will be smaller than irreversible process.

$\therefore\ (T_f)_{irr} > (T_f)_{rev}$

Sol 4: (B) $r \propto \frac{1}{\sqrt{M}}$

$$\because\ r = \frac{\text{Volume effused}}{\text{time taken}} = \frac{V}{t}$$

$$\frac{V}{t} \propto \frac{1}{\sqrt{M}}$$

$\therefore$ For same volumes (V constant)

$t \propto \sqrt{M}$

$$\therefore\ \frac{t_1}{t_2}=\sqrt{\frac{M_1}{M_2}}$$

$$t_{He} = t_{H_2}\sqrt{\frac{M_{He}}{M_{H_2}}}$$

$$5\sqrt{\frac{4}{2}} = 5\sqrt{2}s$$

$$t_{O_2} = t = 5\sqrt{\frac{32}{2}} = 20 \text{ s}$$

$$t_{CO} = 5\sqrt{\frac{28}{2}} = 5\sqrt{14} \text{ s}; \; t_{CO_2}$$

$$= 5\sqrt{\frac{44}{2}} = 5\sqrt{22} \text{ s}$$

Sol 5: (C) Let the mass of methane and oxygen is w

Mole fraction of oxygen = $\frac{\frac{w}{32}}{\frac{w}{32}+\frac{w}{16}} \quad \frac{\frac{1}{32}}{\frac{1}{32}+\frac{1}{16}}$

$$= \frac{\frac{1}{32}}{\frac{3}{32}} = \frac{1}{3}$$

Let the total pressure be P

The pressure exerted by oxygen (partial pressure)

$= X_{O_2} \times P_{total}$

$\Rightarrow P \times \frac{1}{3}$, Hence, (C) is correct.

Sol 6: (A) PV = nRT

$3170 \times 10^{-3} = n \times 8.314 \times 300$

$$n = \frac{3170 \times 10^{-3}}{8.314 \times 300}$$

$V = 1 \text{ Lt} = 1 \text{ dm}^2 = 10^{-3} \text{ m}^3$

$n = 1.27 \times 10^{-3}$ mol

Sol 7: (A) When average speed of molecule is increased due to increase in temperature then the change in momentum during collision between wall of container and molecules of gas also increases.

Sol 8: (C) $\frac{u_{H_2}}{u_{O_2}} = \sqrt{\frac{T_{H_2}}{M_{H_2}} \cdot \frac{M_{O_2}}{T_{H_2}}}$

$$= \sqrt{\frac{50}{2} \cdot \frac{32}{800}} = 1$$

Sol 9: (B) Most probable velocity increase and fraction of molecule possessing most probable velocity decrease.

Sol 10: (C) Vander Waals equation for non-ideal gas

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

Sol 11: (B) Ideal gas has no attractive force between the particles.

Sol 12: (A) Vander Waal's constant for volume correction b is the measure of the effective volume occupied by the gas molecule.

Sol 13: (D) We know that

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

$$\Rightarrow 0.5 = \frac{100 \times V}{0.0821 \times 273}$$

$\Rightarrow$ V = 0.112 litre

According to vander waal's equation

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

$$\left(100 + \frac{a}{(0.112)^2}\right)(0.112 - 0) = 0.0821 \times 273$$

$a = 1.253 \text{ L}^2 \text{ mol}^{-2}$ atm

Sol 14: (A) Average kinetic energy $\propto$ (T Kelvin)

(Factor) $\frac{K.E_2}{K.E_1} = \frac{T_2}{T_1}$

$$= \frac{40+273}{20+273} = \frac{313}{293}$$

Sol 15: (A) Root mean square speed

$$= \left[\frac{n_1C_1^2 + n_2C_2^2 + n_3C_3^2 + \ldots}{n_1 + n_2 + n_3 + \ldots}\right]^{1/2}$$

Sol 16: (C)

$$n = \frac{PV}{RT} = 128 \times 10^{-5} \text{ moles}$$

$$= \frac{3170 \times 10^{-5} \text{ atm} \times 1\text{L}}{0.0821 \text{ L atm k}^{-1} \text{ mol}^{-1} \times 300\text{K}} = 1.27 \times 10^{-3} \text{ mol}$$

Sol 17: (C) Ease of liquefaction $\propto \frac{a}{b}$

For ethane a = 5.49, b=0.0638

For Cl_2 a = 6.49, b = 0.0562

Sol 18: (B) C* = Most probable speed = $\sqrt{\frac{2RT}{M}}$

$\bar{C}$ = Average speed = $\sqrt{\frac{8RT}{\pi M}}$

C = Mean square speed corrected as rms = $\sqrt{\frac{3RT}{M}}$

C* < $\bar{C}$ <C

C* : $\bar{C}$: C = 1 : $\sqrt{\frac{4}{\pi}}$: $\sqrt{\frac{3}{2}}$ =1: 1.128: 1.225

Note: As no option correspond to mean square speed, it is understood as misprint. It should be root Means square speed.

Sol 19: (B) Compressibility factor $(Z) = \frac{PV}{RT}$

(For one mole of real gas)

van der Waal equation

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

At low pressure

V-b ≈ V

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

$$PV+\frac{a}{V} = RT$$

$$PV = RT-\frac{a}{V}$$

$$\frac{PV}{RT} = 1-\frac{a}{VRT}$$

So, $Z = 1-\frac{1}{VRT}$

Sol 20: Initial moles = final moles

$$\frac{P_i \times V}{RT_1}+\frac{P_i \times V}{RT_1} = \frac{P_f \times V}{RT_2}+\frac{P_f \times V}{RT_1}$$

$$\frac{P_i}{T_1}+\frac{P_i}{T_1} = \frac{P_f}{T_2}+\frac{P_f}{T_1}$$

$$\frac{2P_i}{T_1} = P_i\left[\frac{1}{T_2}+\frac{1}{T_1}\right]$$

$$\frac{2P_i}{T_1} = P_f\left[\frac{T_1+T_2}{T_1T_2}\right]$$

$$P_f = 2P_i\left[\frac{T_2}{T_1+T_2}\right]$$

JEE Advanced/Boards

Exercise 1

Sol 1: $NaN_3 \xrightarrow{\quad} \frac{3}{2} N_2 + Na$

125 g NaN_3 mass of NaN_3 = 23 + 14 × 3 = 42 + 23 = 65

$\therefore$ Moles of NaN_3 = $\frac{125}{65}$

Moles of N_2 formed = $\frac{125}{65} \times \frac{3}{2} = \frac{375}{130}$

756 torr = $\frac{756}{760}$ atm

$\therefore$ Volume occupied by N_2PV = nRT

$$\frac{756}{760} \times V = \frac{375}{130} \times 0.0821 \times 300$$

V = 71.42 L

Sol 2: We know, V remains constant

and if P is same

Then, $n_1T_1 = n_2T_2$

$$\Rightarrow \frac{3.6}{44} \times T = \frac{(3.6-0.6)}{44} \times (T + 15)$$

3.6 T = 3T + 45

0.6T = 45

$T = \frac{45}{0.6}$

T = 75 K

$P \times 8 = \frac{3.6}{44} \times 0.0821 \times 75$

P = 0.062 atm

Sol 3: Mole use 0.2 dm^3 O_2 per hour at atm and 273 K per Kg of body

$C_6H_{12}O_6 + 6O_2 \longrightarrow 6\,CO_2 + 6\,H_2O$

For a 1 kg body moles of air (O_2) used,

PV = nRT

$1 \times 0.2 = n \times 0.0821 \times 273$

$\Rightarrow n = 8.923 \times 10^{-3}$

For a 60 kg body moles of O_2 used

$\Rightarrow 60 \times 8.923 \times 10^{-3}$

$\therefore$ Moles of glucose used = $\frac{60 \times 8.923 \times 10^{-3}}{6}$

$n' = 8.923 \times 10^{-2}$

Mass of glucose used

$= 180 \times n' = 16.06$ g

1 mole of O_2 produces, mole of CO_2 and rest condition of temperature and pressure are same

$\therefore$ Volume of CO_2 produced

= Volume of O_2 used

$= 0.2 \times 60 = 12$ dm^3

Sol 4: T = 200 K, P = 8.21 atm

$8.21 \times V = 0.821 \times n \times 200$

$V = 2n$

$\Rightarrow V^2 = 4n^2$

$\therefore$ Slope is constant slope = 1/4

$x = 4y \Rightarrow y = \frac{x}{4}$

Sol 5:

$$\begin{array}{llll} 2NH_3 & \longrightarrow & N_2 & +\ 3H_2 \\ a\text{-}x & & x/2 & 3x/2 \end{array}$$

$P_1 = 760$ mm = 1 atm

After sparking $\longrightarrow$ due to reaction, number of moles increases.

$\therefore$ pressure gas (V and T are constant)

$\therefore P_2 = 760 + 190 = \frac{950}{760}$ atm

$P \propto n$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$\frac{760}{950} = \frac{a}{a + \frac{3\alpha}{2} + \frac{\alpha}{2} - \alpha}$$

$$\frac{760}{950} = \frac{a}{a+\alpha}$$

$$\therefore \alpha = \frac{190}{760}$$

$\therefore$ % dissociation α

$= \frac{190 \times 100}{760} = 25\%$

Sol 6: $2H_2\,(g) + O_2(g) \longrightarrow 2H_2O(g)$

$$n_{H_2} = \frac{10^{-2} \times 10^3}{2} = \frac{10}{2} = 5 \text{ moles}$$

$$n_{O_2} = \frac{6.4 \times 10^{-2} \times 10^3}{32} = \frac{64}{32} = 2 \text{ moles}$$

$\therefore$ Total moles of ideal gas = 7

$V = 10 \times 10^{-3}$ m^3

T = 473 K

R = 8.314 J / mol / K

$$\therefore P = \frac{nRT}{V} = \frac{7 \times 8.314 \times 473}{10^{-2}} \text{ Pa}$$

P = 27.54 bar

If the mixture ignites and the reaction complexes,

For $H_2 = \frac{N}{v} = \frac{5}{2} = 2.5$

For $O_2 = \frac{2}{1} = 2$

$\therefore O_2$ is limiting reagent

Number of moles of H_2 left after reaction = $5 - 2 \times 2 = 1$

Number of moles of H_2O formed = $2 \times 2 = 4$

$\therefore$ Total moles of ideal gas = 1 + 4 = 5

$$\therefore \frac{P_i}{Pt} = \frac{7}{5}$$

$$P_t = \frac{5}{7} P_i = \frac{5}{7} \times 27.54 \text{ bar} = 19.67 \text{ bar}$$

Sol 7: (i) Under similar condition of P and T

$$r \propto \frac{1}{\sqrt{\text{Molecular weight}}}$$

$$\frac{r_{SO_2}}{r_{CH_4}} = \sqrt{\frac{64}{16}}$$

$$\left(\frac{r_{SO_2}}{r_{CH_4}}\right) = 2:1$$

(ii) A container contains SO_2 and CH_4 in ratio 3 : 2

$$\frac{w_{SO_2}}{w_{CH_4}} = \frac{3}{2}$$

$$\therefore \frac{n_{SO_2}}{n_{CH_4}} \times \frac{64}{16} = \frac{3}{2}$$

$$\therefore \frac{n_{SO_2}}{n_{CH_4}} = \frac{3}{8}$$

We know partial pressure of a gas ∝ molar fraction of gas

$$\therefore \frac{P_{SO_2}}{P_{CH_4}} = \frac{n_{SO_2}}{n_{CH_4}} = \frac{3}{8}$$

We know, $r \times \frac{P}{\sqrt{M.w.}}$

$$\frac{r_{SO_2}}{r_{CH_4}} = \frac{P_{SO_2}}{P_{CH_4}} \times \sqrt{\frac{M.w._{CH_4}}{M.w._{SO_2}}}$$

$$\frac{r_{SO_2}}{r_{H_4}} = \frac{3}{8} \times \sqrt{\frac{16}{64}} = \frac{3}{16}$$

(iii) After n-steps of effusion,

$$\frac{n_{SO_2}}{n_{CH_4}} = \left(\frac{r_{SO_2}}{r_{CH_4}}\right)^n$$

$$\therefore \frac{n_{SO_2}}{n_{CH_4}} = \left(\frac{8}{1}\right)^{1/n} \quad n = 3$$

$$\therefore \frac{n_{SO_2}}{n_{CH_4}} = 2:1$$

Sol 8: We know $r \propto \frac{1}{\sqrt{M.w.}}$

$$\frac{rate_{mix}}{rate\ of\ O_2} = \sqrt{\frac{M.w.O_2}{M.w._{mix}}}$$

$$\frac{\frac{V_{mix}}{time}}{\frac{V_{O_2}}{time}} = \sqrt{\frac{32}{M_{mix}}}$$

Equal volume are diffused in unequal the

$$\frac{\frac{V}{234}}{\frac{V}{224}} = \sqrt{\frac{32}{M_{mix}}}$$

$$\frac{224}{234} = \sqrt{\frac{32}{M_{mix}}}$$

$\therefore M_{mix} = 34.92$

Mass of mixture containing 50% O_2 and 20% other gas with molecular weight m.

$$\therefore M_{mix} = \frac{80 \times 32 + 20 \times m}{100}$$

34.92 × 100 = 2560 + 20 m

$$\frac{932}{20} = m$$

M = 46.6

Sol 9: We know, V = 3; P = 24.6

T = 300 K

24.6 ×3 = 0.082 × 300 × x

∴ n = 3 mole

1 mole of O_2 and 2 moles of H_2

∴ Partial pressure of both gases are in the ratio 2 : 1

We want finally

$$\frac{w_{D_2}}{w_{H_2}} = \frac{1}{4}$$

$$\frac{n_{D_2} \times 2}{n_{H_2} \times 1} = \frac{1}{4}$$

$$\therefore \frac{n_{D_2}}{n_{H_2}} = \frac{1}{8}$$

We know

$$\frac{n_{D_2}}{n_{H_2}} = \left(\frac{r_{D_2}}{r_{H_2}}\right)^n \text{ and } \frac{r_{D_2}}{r_{H_2}} = \frac{P_{D_2}}{P_{H_2}} \sqrt{\frac{M.w.H_2}{M.w.D_2}} = \frac{1}{2}\sqrt{\frac{2}{4}} = \frac{1}{2}\sqrt{\frac{2}{2}}$$

$$\frac{1}{8} = \left(\frac{1}{2\sqrt{2}}\right)^{(n-1)}$$

∴ n = 3

$(2)^{-3} = 2^{-\frac{3}{2}}$

n = 2

Sol 10: P = 250 kPa

T = 300 K

Using, PV = nRT

V moles remain constant

$\therefore$ Point when cylinders blows up,

P = 10^6 Pa

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

$$\frac{250\times 10^3}{300} = \frac{10^6}{T_2}$$

$$\Rightarrow \quad T_2 = \frac{10^6 \times 300}{250\times 10^3} = 1200 < 1800$$

$\therefore$ The cyclinder will blow up before it melts.

Sol 11: Density = 0.00009 g/cc

= 0.00009 × 10^3 kg/nm

$$U_{r.m.s.} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{P}} = \sqrt{\frac{3\times 1\times 1.0323\times 10^3}{0.09}}$$

PM = ρRT

$$\frac{RT}{M} = \frac{P}{\rho}$$

$u_{r.m.s.}$ = 1838 m/s = 183800 cm/s

Sol 12: V = 1 dm^3 = 10^{-3} m^3

M.w. = 2 × 10^{-3} g

P = 101.325 kPa

1.03 × 10^{23} H_2 molecules

$\Rightarrow$ Number of moles

$$= \frac{\text{Number of molecules}}{\text{NA}} = \frac{1.03}{6.023}$$

$$101.325 \times 10^3 \times 10^{-3} = 8.314 \times \frac{1.03}{6.023} \times T$$

$\therefore$ T = 71.27 K

$$u_{avg} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times 8.314\times 71.27}{3.142\times 2\times 10^{-3}}}$$

u_{avg} = 868.53 m/s

Sol 13: T = 273 K, P = atm

Density = 1.2505 kg/m^3

M = 12 + 16 = 28

$$\text{R.M.S.} = \sqrt{3\frac{P}{D}} = \sqrt{\frac{3\times 1.01325\times 10^5}{1.2504}}$$

$u_{r.m.s.}$ = 493.05 $\approx$ 493 m/s

We know

$$u_{avg} = \sqrt{\frac{8}{\pi}\times\frac{1.01323\times 10^5}{1.2504}}$$

u_{avg} = 454.37

$$u_{mp} = \sqrt{\frac{2P}{D}} = \sqrt{\frac{2}{3}}\ \mu r_{.m.s.}$$

u_{mp} = 402.63 $\approx$ 403

Sol 14: Fraction of molecules in the range

μ_P 0.005 m/s to μ_P to 0.005 m/s

$$\frac{dNu}{N} = 4\pi\left[\frac{M}{2\pi RT}\right]^{-3/2} e^{-\frac{Mu^2}{2RT}}\ u^2du$$

We know $u^2 = \frac{2RT}{M}$ and

du = 0.005 × 2 = 0.01

$\therefore$ Fraction of moles

$$\text{Frac} = 2\pi \times \frac{M}{2\pi RT} \times \left(\frac{M}{2\pi RT}\right)^{1/2} \times e^{-1} \times \frac{2RT}{M}\ du$$

$$\text{Frac} = \frac{4x}{e}\left(\frac{M}{2\pi RT}\right)^{1/2} \times 0.01 \times \text{ups}$$

$$= \frac{4}{e} \times \left(\frac{M}{2\pi RT}\right)^{1/2} \times 0.01 \times \left(\frac{2RT}{M}\right)^{1/2}$$

$$= \frac{4}{\sqrt{\pi e}} \times du = \frac{4\times 0.01}{e\times\sqrt{\pi}} = 8.304 \times 10^{-3}$$

$$\textbf{Sol 15: } \text{Ratio} = \frac{4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{M(2u)^2}{2RT(2u)^2du}}}{4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mu^2}{2RTu^2du}}}$$

$$U^2 = \frac{2RT}{M}$$

$$\therefore \text{Ratio} = \frac{e^{-\frac{4M}{2RT}\times\frac{2RT}{T}} \times u^2}{e^{-\frac{M}{2RT}\times\frac{2RT}{M}} \times u^2du}$$

$$\text{Ratio} = \frac{e^{-4}}{e^{-1}} \times 4$$

Ratio = 4 × e^{-3}

∴ Ratio = 0.199

Sol 16: R = 8J, NA = 6 × 10^{23}

$V_A = V_B$ = 2 litre = 2 × 10^{-3} m^3

(i) For container A

T = 300 K

N = 6 × 10^{20}

$$\therefore \text{No. of moles} = \frac{6\times10^{20}}{6\times10^{23}} = 10^{-3}$$

$$P_A = \frac{nRT}{V} = \frac{10^{-3}\times8\times300}{2\times10^{-3}} = 1200 \text{ Pa} = 0.012 \text{ atm}$$

(ii) P_B = 1 atm, T = 600 K

$$\therefore n = \frac{PV}{RT} = \frac{1.01325\times10^{5}\times2\times10^{-3}}{48\times600}$$

$$= \frac{1.01325}{24}$$

$$W = n \times N_A = \frac{1.01325}{24.4}\times6\times10^{23}$$

N = 25.33 × 10^{21} = 2.5 × 10^{22}

$$K.E._{avg} = \frac{1}{2} MV\, u^2_{avg} = \frac{1}{2} \times n \times M.w.\, u^2_{avg}$$

$$= \frac{n}{2}\times\frac{M.w.\times8RT}{\pi M.w.}$$

$$K.E._{avg} = \frac{4RTn}{\pi} = \frac{4PV}{\pi}$$

$$\text{(iii) } K.E_A = \frac{uP_AV_A}{\pi} = \frac{4\times1200\times2\times10^{-3}}{3.14} = 3.05 \text{ J}$$

$$\text{(iv) } K.E_B = \frac{4P_BV_B}{\pi} = \frac{105\times2\times10^{-3}\times4}{3.14}$$

KE_B = 258.15 J

$$\text{(v) Ratio of } u_{mps} = \frac{\sqrt{\frac{2RT_A}{M}}}{\sqrt{\frac{2RT_B}{M}}} = \sqrt{\frac{T_A}{T_B}} = \sqrt{\frac{1}{2}}$$

$$Z_{11} = \frac{1}{\sqrt{2}}\ \pi\sigma^2\ cav\rho^2$$

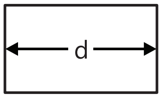
(vi) Ratio of Z_{11}

$$\frac{(Cav\rho^2)A}{(Cav\rho^2)B} = \frac{\sqrt{\frac{8}{\pi}\frac{RT_A}{M}}\times\left(\frac{6\times10^{20}}{V}\right)^2}{\sqrt{\frac{8}{\pi}\frac{RT_B}{M}}\times\left(\frac{2.5\times10^{22}}{V}\right)^2}$$

$$= \sqrt{\frac{T_A}{T_B}}\times\left(\frac{6}{2.5\times100}\right)^2 = \frac{1}{\sqrt{2}}\times\left(\frac{6}{250}\right)^2$$

Ratio = 0.4 × 10^{-3} : 1

Sol 17: No. of wall collision / per unit line of molecules



Let length of container be d and $v_{r.m.s.}$ be V

then time taken for 1 colles Q = $\frac{d}{V}$ s

It collision in 1 sec = $\frac{V}{d}$

If N molecules are present

Then total collision = $\frac{VN}{d}$

We have been given

$$\frac{V_{He}\ N_{He}}{d} = \frac{V_{H_2}\ N_{H_2}}{d}$$

$$\sqrt{\frac{3RT}{M_{He}}}\ N_{HE} = \sqrt{\frac{3RT}{M_{H_2}}} \times N_{H_2}$$

$$\therefore \frac{N_{He/v}}{N_{H_2/v}}\sqrt{\frac{M_{He}}{N_{H_2}}} = \sqrt{2} > 1$$

$$\frac{N_{He}}{V} > \frac{N}{V}\ H_2$$

Conc. of He > Conc. of H_2

Sol 18: Mean free path (λ) = 2.6 × 10^{-5} m

(at 300 K)

σ = 0.26 nm

$$\lambda = \frac{KT}{\sqrt{Z}\pi\sigma^2 P}$$

$$\therefore P = \frac{KT}{\sqrt{Z}\pi\sigma^2\lambda}$$

$$K = \frac{R}{N_A}$$

$$\therefore P = \frac{R\times T}{N_A\sqrt{2}\pi\sigma^2\lambda}$$

$$\frac{8.314\times 300}{6.023\times10^{23}\times\sqrt{2}\pi\times(0.26\times10^{-10})\times2.6\times10^{-5}} = \frac{2494.2}{4700.86}$$

$\therefore$ P = 5.30 × 10^2 Pa

PV = nRT

P = cRT

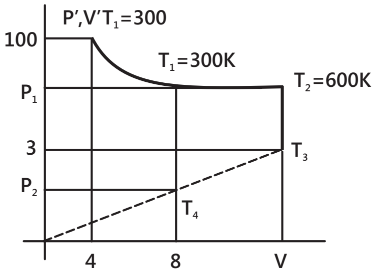
5.30 × 10^2 = C × 8.314 × 300

$\therefore$ c = 2.12 × 10^{-3}

No. of molecules / volume

= c × NA = 1.28 × 10^{21} molecule/ vol

Sol 19:



In the constant temperature curve,

T_1 = 300 K

P = 10, V = 4

10 × 4 = 300 × 0.081 × n

$\therefore$ n = 1.624

(i) At T_1 = 300 K

Using $P_1V_1 = P'\,V'$

P_1 × 8 = 10 × 4

P_1 = 5

(ii) $T_2 - T_3$ constant

$$\therefore \frac{P_1}{T_2} = \frac{3}{T_3}$$

$$\frac{5}{600} = \frac{3}{T_3}$$

$\therefore$ T_3 = 360 K

(iii) At T_2 = 600 K, P = 5 atm

T_1 & T_2 constant present

$$\frac{600}{V_1} = \frac{300}{8}$$

$\therefore$ V_1 = 16

(iv) $T_3 \to T_4$

$P \propto V$

(v) $\frac{3}{V_1} = \frac{P_2}{8} \Rightarrow$ P2 = 1.5

$$\frac{3}{16} = \frac{P_2}{8}$$

$$\frac{1.5\times8}{T_4} = \frac{3\times16}{T_3}$$

$$T_4 = \frac{T_3}{4}$$

$$T_4 = \frac{360}{4} = 90$$

T_4 = 90

Sol 20: Balloon initially contain 1 mole air at 1 atm balloon filled till P_f = 3 atm

(a) $P \propto r$

P_{final} = 3 atm

$$d_f = \frac{P_f\times d_i}{P_i}$$

$$d_f = \frac{3\times1}{1} = 3\text{m}$$

$$\therefore \frac{P_iV_i}{n_i} = \frac{P_fV_f}{T_f}$$

Temperature is same

$$\frac{1\times\frac{4}{3}\pi\times(r_1)^3}{1} = \frac{3\times\frac{4}{3}\pi\times(r_f)^3}{n_f}$$

$$N_f = 3\left(\frac{r_f}{r_i}\right)^3 = 3\times3^3$$

N_f = 81

Number of moles of air added = 81 – 1 = 80

(b) If p_{final} = 7 atm,

Then $r_{final} = \frac{7}{2}$ m

$\therefore V = \frac{4}{3}\pi \times \left(\frac{7}{2}\right)^3 = 57.166\ \pi > 36\ \pi$

$\therefore$ If volume increases greater than 36 πm^3 balloon burst

At V = 36 π

$\frac{4}{3}\ \pi r^3 = 36\ \pi$

$\therefore r = 3$

$\therefore P = 6$ atm

$$\frac{6 \times 36\pi}{n_f} = \frac{1 \times \frac{4}{3}\pi\left(\frac{1}{2}\right)^3}{1}$$

$$n_f = \frac{6 \times 36}{\frac{1}{6}}$$

$\therefore$ Number of extra moles added = 1296 – 1 = 1295

Sol 21: $NH_4Cl \xrightarrow{\quad} NH_3(g) + HCl(g)$

1 mole 1 mole 1 mole

T = 600 K

V = 24.63

N = 2 moles

$\therefore P_{developed} = \frac{nRT}{V} = \frac{2 \times 0.0821 \times 600}{24.63}$

$P_{developed} = 4$

$P_{difference} = 4 - 1$

= 3 atm < 5.5

$\therefore$ The lid does not bounce off

Sol 22: b = 39.1

P = 10^{-3} mm Hg = 1.316×10^{-6} atm

= 0.133 Pa

T = 298 K

M = 28×10^{-3}

$4 \times N_A \times V_{molecule} = b$

$4 \times 6.023 \times 10^{23} \times \frac{4}{3}\pi r^3 = 39.1\ cm^3$

$\therefore$ r = 1.57 Å

$\sigma = 2r = 314$ pm

$$\lambda = \frac{KT}{\sqrt{Z}n\sigma^2 P} = \frac{RT}{N_A\sqrt{Z}n\sigma^2 P}$$

$$= \frac{8.314 \times 298}{6.023 \times 10^{23} \times \sqrt{2} \times \pi \times (314 \times 10^{-12})^2 \times 0.133}$$

$$= \frac{2477.57}{35072.639}$$

$\lambda = 0.0701$ m

$\lambda = 7.051$ m

$$C_{avg} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 298}{3.14 \times 28 \times 10^{-3}}}$$

= 474.8 m/s = 47480.39 m/s

$Z_1 = \sqrt{2}\ \sigma\pi^2 C_{av} p$

We know, PV = nRT

$0.133 \times V = 8.314 \times n \times 298$

$\therefore \frac{n}{V} = 5.36 \times 10–5$

$$P = \frac{\text{Number of molecule}}{\text{Volume}} = \frac{nN_A}{V}$$

= 3.233×10^{19} molecules/m^3

$Z_1 = \sqrt{2}\ \pi\sigma^2 C_{qv} \times P$

$= \sqrt{2} \times \pi \times (3.14 \times 10^{-12})^2 \times 474.80 \times 3.023 \times 10^{19}$

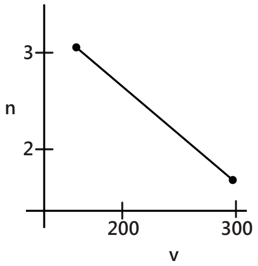
$\Rightarrow Z_1 = 6742\ s^{-1}$

$$Z_{11} = \frac{Z_1 \times p}{Z}$$

$$= \frac{6742 \times 3.023 \times 10^{19}}{2} = 1.017 \times 10^{23}\ m^3/s$$

= $1.017 \times 10^{25}\ cm^3/s$

Sol 23:



N = mT + c

(3 = m × 200 + c)

(2 = m × 300 + c) × 2

$9 - 4 = c$

$\therefore c = 5$

`3 = 200m + 5

$\therefore m = \frac{-1}{100}$

$\therefore n = 5 - \frac{T}{100}$

PV = nRT

$1 \times V = R\left(5 - \frac{T}{100}\right) \times T$

$V = 5RT - \frac{RT^2}{100}$

$\frac{2V}{2T} = 5R - \frac{2RT}{100} = 0$

at $T = \frac{500}{2} = 250$ K

$\therefore V_{max/mix} = R\left(5 - \frac{250}{100}\right) \times 250 = 51.312$ litre

Sol 24: $A(g) \longleftrightarrow A_2\,(g)$

M.Weight 48 96

V = 33.6 litre

T = 273ºC = 546 K

Given 50% of weight is dimer

$\therefore$ Mass of dimer = 0.5 × 96

$\therefore$ Moles of dimer $= \frac{0.5 \times 96}{96} = 0.5$

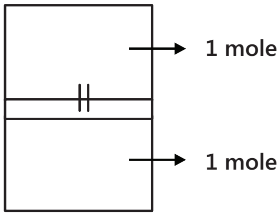
Moles of monomer $= \frac{96 \times 0.5}{48} = 1$

Total moles = 1 + 0.5 = 1.5

$\therefore P = \frac{nRT}{V} = \frac{1.5 \times 0.0821 \times 546}{33.6}$

$P = 1.998 \approx 2$

Sol 25:



Moles are same

$P_{lower} = P_{upper} + P_{friction}$

Using, $P_v V_v = P_L V_L$

$\frac{P_{upper}}{P_{lower}} = \frac{1}{4}$

$\frac{P_{upper}}{P_{upper} + P_{piston}} = \frac{1}{4}$

$\therefore P_{piston} = 3P_{upper}$ 1

$P_{lower\ final} = P_{upper\ final} + P_{piston}$

$\frac{P_{Lower}}{P_{upper}} = \frac{V_{upper}}{V_{lower}}$

$\frac{P_{upper} + P_{piston}}{P_{upper}} = 3$

$\therefore 2P_{upper\ final} = 2P_{piston}$

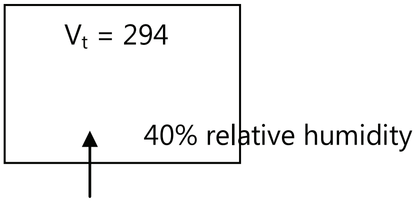
$\therefore P_{upper\ final} = \frac{3}{2} P_{upper\ initial}$

Using $\frac{PV}{T}$ balance for upper chamber

$\frac{P_{upper} \times 0.8V}{300} = \frac{3}{2}\frac{P_{upper} \times 0.75V}{T_f}$

$T_f = \frac{3}{2} \times \frac{3}{4} \times \frac{300}{0.8} = 421.875$ K

Sol 26:



At 21ºC $P \approx 19$ torr

40% humidity,

$\therefore$ P due to $H_2O = 0.4 \times n = \frac{0.4 \times 19}{760}$ atm = 0.01 atm

R = 0.082; T = 294 K

0.01 × 294 = 0.082 × 294 × n

$\therefore$ n = 0.123

$\therefore$ 0.122 moles of water added/minutes

Mass of H_2O = 2.215g of H_2O added/min

$\approx$ 2.2g

Sol 27: If theoretical is correct

Than $\frac{1.54}{3.2} = \frac{T+273}{T+10+273}$

$\therefore \frac{1.54}{3.2-1.54} = \frac{T+273}{10}$

Theoretical T′ = – 263.72 °K

(a) Real case

$$\frac{1.25}{2.2875} = \frac{T'+273}{T'+10+273}$$

$$\frac{1.25}{2.2875-1.25} = \frac{T'+273}{10}$$

T′ = 12.048 K

Using $\frac{P}{nT}$ balance between theoretical and real

$$\frac{1.54}{9.27 \times n_{theoretical}} = \frac{1.25}{12.048 \times n_{Actual}}$$

$$\therefore \frac{n_{exp}}{n_{case}} = \frac{1.25 \times 9.27}{12.048 \times 1.54} = 0.624$$

$nA \longrightarrow$ A 50% yield

$$\frac{n_A}{2} \qquad \frac{n_{theor}}{n} \times 2$$

$$\text{Total} = n_{exp} = \frac{n_A}{2} + \frac{n_A}{2n}$$

$$\frac{\frac{n_A}{2} + \frac{n_A}{2n}}{n_A} = 0.625$$

(b) $\frac{1}{2n} = 0.625 - 0.5; \quad n = \frac{1}{2 \times (0.625 - 0.5)} = 4$

Sol 28: $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

3 times O_2 theoretical is required for optimal fuel

$\therefore$ For optical fuel, $\frac{n_{CH_4}}{n_{O_2}} = \frac{1}{2 \times 3} = \frac{1}{6}$

We know,

$$\frac{r_{CH_4}}{r_{O_2}} = \frac{n_{CH_4}}{n_{O_2}} \times \sqrt{\frac{M_{O_2}}{M_{CH_4}}}$$

$$\therefore \frac{1}{6} = \sqrt{\frac{32}{16}}$$

$$\frac{1}{6} = \frac{1}{192} \times (\sqrt{2})^n; \ \frac{192}{6} = (\sqrt{2})^n$$

$32 = (\sqrt{2})^n$

$\therefore$ n = 10 steps

Let initial moles be n_A, n_B

$\therefore$ After 1 effusion

$$\frac{n_A}{n_B} = \frac{n_{A_i}}{n_{B_i}} \times (\sqrt{2})$$

And 90% of n_A is remove

$$\therefore \frac{n_A}{n_O} = \frac{n_{A_i}}{n_{B_i}} \times (\sqrt{2}) \times (0.9)$$

$\therefore$ After 10 steps,

We know

1 mole CH_4 produces 100 – fours

$\therefore$ To produces

$$\frac{1}{3} = \frac{n_{A_i}}{n_{B_i}} \times (\sqrt{2}\,x)$$

$$\therefore \frac{1}{6} = \frac{n_{A_i}}{n_{B_i}} \times 32\,x$$

$$\therefore \frac{n_{A_i}}{n_{B_i}} = \frac{1}{32}$$

Also to produce 1000 cal, 10 moles of CH_4 is begin

$\therefore 10 = n_{CH_4} \times (0.9)^{10}$

$\therefore n_{CH_4} = 27.78$ mole

Moles of O_2 = 2778 × 3 × 0.36 × 32

= 5333.33 moles

Sol 29:

V 50

V_1=50/3	V_2=50/3	V_3=50/3
60 H_2 N = 30 mole	160g O_2 n_{O_2} = 5 ml	100g N_2 n_{N_2} = 5 noes

The SPN will permit the flow of N_2 or H_2 till the concentrations in chambers are equal (As volume is same for all chambers)

∴ At equilibrium

Moles of H_2 in all 3 chambers is same n_{H_2} in each chamber

$$= \frac{30}{3} = 10 \text{ moles in each}$$

In light and middle chamber, number of moles of N_2 must be same.

∴ Total number of moles of N_2 in both chambers = $\frac{5}{2}$ = 2.5

∴ Total number of moles in each chamber

Left = moles of H_2 = 10

Right = moles of N_2 + moles of H_2 = 2.5 + 10 = 12.5

Middle = moles of O_2 + moles of N_2 + moles of H_2 = 5 + 2.5 + 10 = 17.5

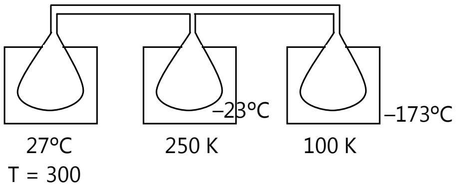
We know, volume and temperature are same

$\therefore P \propto n$

$\therefore P_L : P_M : P_R = nL : nM : nR$

= 10 : 17.5 : 12.5 = 4 : 7 : 5

Sol 30: Volume of all bulbs = 1 litre



$$P_i = \frac{547.2}{760}$$

$$n_i = \frac{P_i V_i}{Rt_i} = \frac{0.72 \times 1}{0.821 \times 300} = 0.029$$

(a) **Case-1**

A and B are connected

P = 228 mn Hg = 0.3 atm

V = 1 ℓ

T_A = 300 k

$$\therefore n_A = \frac{PV}{RT} = \frac{0.3 \times 1}{0.821 \times 300} = 0.0122$$

$$n_B = \frac{P_B V_B}{RT_B} = \frac{0.3 \times 1}{0.821 \times 250} = 0.0143$$

(b) n_{total} = 0.0265

$\therefore n_{freezed}$ = 0.029 – 0.026

= 0.0025 moles of H_2O freezed

To be in equilibrium the partial pressure of gases in both bulbs must be same.

∴ All H_2O gets converted to solid as it keeps flowing to bulbs 2 to achieve equilibrium

∴ Moles of $H_2O = 2.5 \times 10^{-3}$

(c) Both stopcocks are opened

Now since CO_2 gets solidified in bulbs C, the entire CO_2 solidifies in bulbs C.

$P_{\text{at equilibrium}}$ = 45.6 mm of Hg

$$= \frac{45.6}{760} = 0.06 \text{ atm}$$

0.06 × 1 = 0.0821 × 300 × n

$\therefore n_A = 2.536 \times 10^{-3}$

$$n_B = \frac{PV}{RT} = \frac{0.06 \times 1}{0.0821 \times 250} = 2.923 \times 10^{-3}$$

$$n_c = \frac{PV}{RT} = \frac{0.06 \times 1}{0.082 \times 100} = 7.3038 \times 10^{-3}$$

Exercise 2

Single Correct Choice Type

Sol 1: (C) Suppose initial ratio is represented by n_0

$$\frac{r_1}{r_2} \propto \frac{n_1^0}{n_2^0}\sqrt{\frac{M_2}{M_1}}$$

$$\frac{n_1^1}{n_2^1} \propto \frac{n_1^0}{n_2^0}\sqrt{\frac{M_2}{M_1}}$$

n^{th} step ratio of moles

$$\frac{n_1^n}{n_2^n} = \frac{n_1^0}{n_2^0}\left(\sqrt{\frac{M_2}{M_1}}\right)^n$$

$$\therefore \frac{3072/2}{20/32} = \frac{240/2}{160/32}\left(\sqrt{\frac{32}{2}}\right)^n$$

$1024 = 4^n$

n = 5

Sol 2: (B) $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$

(a) $\frac{r_A}{r_B} = \sqrt{\frac{28}{28}} = 1$

(b) $\frac{r_{O_2}}{r_{O_3}} = \sqrt{\frac{48}{32}} = \sqrt{\frac{3}{2}}$

(c) $\frac{r_{UF_{235}}}{r_{UF_{238}}} = \sqrt{\frac{238}{325}}$

b > c > a

Sol 3: (C) MA = 4 MB = 40

Let weight be x_g each

Mole fraction of M_A

$$= \frac{n_A}{n_A + n_B} = \frac{\frac{x}{M_A}}{\frac{x}{M_A} + \frac{x}{M_B}}$$

$\therefore$ Partial pressure of A (lighter)

= Mole fraction × P

$= \frac{1}{1.1} \times 1.1 = 1$ atm

Sol 4: (C) PV = nRT

$\Rightarrow PV = \frac{m}{M} RT \quad M$ = Molar mass

$\Rightarrow PV = \frac{dV}{M} RT \quad d$ = Density

$\Rightarrow PM = dRT$

$$\frac{P_A}{P_B} = \frac{\frac{d_A T_A}{M_A}}{\frac{d_B T_B}{M_B}}$$

$$\Rightarrow \frac{\frac{2d_B T_B}{M_A}}{\frac{d_B T_B}{3M_A}} \Rightarrow 6 : 1$$

Sol 5: (C) $2NH_3(g) \longrightarrow N_2 + 3H_2$

$\frac{r_{SO_2}}{r_{mix}} = \frac{1}{2}$

$\sqrt{\frac{M_{mix}}{M_{SO_2}}} = \frac{1}{2}$

Or rate of diffusion $\propto \frac{1}{\sqrt{M}}$

$\Rightarrow M_{mix} = \frac{M_{SO_2}}{4} = \frac{32+32}{4}$

$M_{mix} = 16$

Let 'x' fraction NH_3 converts to N_2 and H_2'

$\Rightarrow M_{mix} = 2(1 - x) \times 17 + 3x \times 2 + 28 \times x$

$16 = \frac{34 - 34x + 34x}{2(1-x) + 3x + x}$

$16 = \frac{34}{2 + 2x}$

32 + 32x = 34

32x = 2

$X = \frac{2}{32} = \frac{1}{16}$

% convert to $= \frac{100}{16} = 6.25\%$

Sol 6: (B) $3A \longrightarrow 2B$

V = 0.0821 ℓ

Initially n_A = 1 Mole

Let degree of dissociation be x%

$\Rightarrow 3A \longrightarrow 2B$

$1–3x \longrightarrow 2x$

$\therefore$ Total moles = 1 – 3x + 2x = 1 – x

We know PV = nRT

P × 0.0821 = 1 – x × 0.0821 × 7

We know slope = tan(angle between P–T curve)

= tan(42.95°) = 0.8

$\Rightarrow 1 - x = 0.8$

$\Rightarrow x = 0.2$

% percentage conversion

$$= \frac{n_{A_{initial}} - n_{A_{final}}}{n_{A_{initial}}} = \frac{1 - (1 - 3 \times 0.2)}{1}$$

= 3 × 0.2 = 0.6

Sol 7: (B) For a balloon,

$P_1V_2 = nRT_1$

$20 \times 2.82 = n_{vessel} \times 0.0821 \times 300$

$\Rightarrow n_{H_2}$ in vessel = 2.29

n_{H_2} is one balloon

$$1 \times \frac{4}{3}\pi \times \left(\frac{21}{2}\right)^3 \times 10^{-3}$$

$= n_b \times 0.0821 \times 273$

$\Rightarrow$ Total number of balloon N

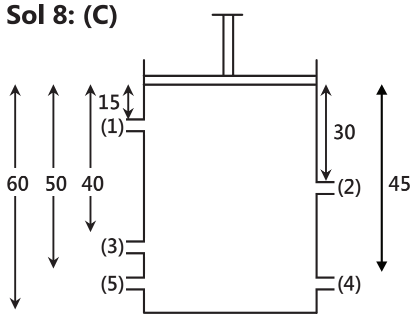
We know $N \times n_b = n$ used

$$N = \frac{n_{vessel}}{n_B} = \frac{2.29}{0.216}$$

N = 10.56

N ≈ 10 balloon

Sol 8: (C)



Volume initial = 821×60 cm^6

P = 1 atm

T = 300 K

$1 \times 821 \times 60 \times 10^{-3} = 0.821 \times 300 \times 4$

$$n = \frac{821 \times 6 \times 10^{-2}}{3 \times 8.21} \qquad \therefore n = 2 \text{ initially}$$

Using PV balance

$P_1V_1 = P_2V_2$

$\therefore 1 \times 60 \times 821 = P_2 \times 821 \times (60 - x)$

$$\therefore P_2 = \frac{60}{60 - x}$$

$\therefore$ At x = 15

$P_2 = 60/45 = 4/3 < 1.3$

Valve - 1 does not open

At x = 30

$$P_2 = \frac{60}{30} = 2 < 2.2$$

Valve-II does not open

At x = 40

$$P_2 = \frac{60}{20} = 3 > 2.5$$

$\therefore$ Before reaching

Valve 3 $\rightarrow$ Opens as V-3 opens

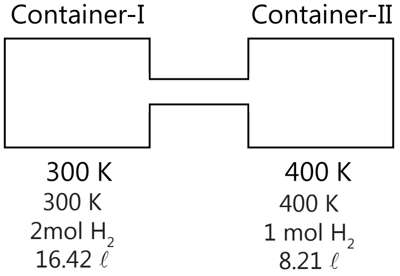
P = 1 atm

$$V = \frac{V_{initial}}{3}$$

$$\text{So, } n = \frac{2}{3} \text{ mole}$$

Multiple Correct Choice Type

Sol 9: (B, D)



$P_I \times 16.42 = 0.0821 \times 300 \times 2$

$P_{I_{initial}} = 3$ atm $P_{II_{initial}} = 4$ atm

After opening the valve (to reach equilibrium), pressure & temperature in compartment must be same

$3 < P_{final} < 4$

PV = nRT

After opening valve, P_{final}, T_{final} will be same in both container

$P_{I_{final}} = P_{II_{final}} = P_{final}$

$P_f(16.42 + 8.21) = (2 + 1)(0.0821)T_f$

$T_f = x_I T_I + x_{II} T_{II} = 357$ K

$P_f = 3.57$ atm

Sol 10: (A, D) V = 8.21 ℓ, n = 2 moles T = 300 K

$$P = \frac{nRT}{V} = \frac{0.0821 \times 2 \times 300}{8.21}$$

P = 6 atm

If the container is open

Then P ∝ nT and P ∝ T (is wrong) hence statement B is incorrect

Similarly if container is closed-non-rigid.

PV ∝ T and not V ∝ T

If another container is introduced,

P must be same

$\therefore n_1T_1 = n_2T_2$

$n \times 300 = (2 - n) \times 150$

$2n = 2 - n$

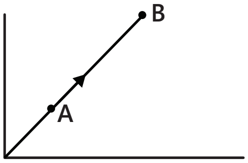
$\Rightarrow n = 2/3$

$$\frac{P_{final}}{P_1} = \frac{n_f}{n_I}$$

(all other parameter constant)

$$P_{final} = \frac{2}{3} \times P_{initial} = \frac{2}{3} \times 6 = 4 \text{ atm}$$

Sol 11: (A, B)



As you can see, P – T curve is a straight line passing through origin

Hence P ∝ T

P = nT

and we know PV = nRT

mV = n

Hence if n changes, V also changes and vice-versa

If n = Constant

then V = Constant

Sol 12: (B, D) Pi = 76 cm of Hg = 1 atm

PA = 1 atm

$$2A\ (g) \longrightarrow 3B\ (g) + 2C\ (g)$$

1 – 2x 3x 2x

$P_{A_{final}} = 0.8$

1 – 2x = 0.8

$\Rightarrow x = 0.1$

$P_B = 3 \times 0.3 = 0.3$

$P_C = 2 \times 0.1 = 0.2$

$\Rightarrow P_{total} = 0.8 + 0.2 + 0.3 = 1.3$ atm

$P_{increase} = 0.3$ atm $= 0.3 \times 760 = 228$ mm of Hg

Sol 13: (A, B, D) Total area under the curve is integration of fraction of molecules with all possible speed

⇒ Total area = 1 (in dependent of T and molecule weight of gas)

As temperature increases u_{mps} ↑es,

As $\mu_{mps}\ T_2 > \mu_{mps}\ T_1$

$\Rightarrow T_2 > T_1$ (∴ statement-II false)

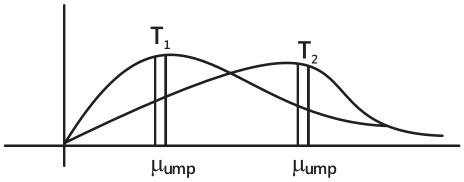
(Statement-II incorrect)

According to the equation, the fraction of molecules with

umps + ½ ump, ump + ½ umps is constant

And fraction $= \dfrac{4f}{\sqrt{\pi e}}$ $\therefore A_1 = A_2$

As temperature ↑es, mole



Fraction of molecules with u_{mps}. Decreases as temperature ↑es.

Sol 14: (A, C) Fraction of molecules with $u_{avg} + fu_{avg}$

$$\int \frac{d_{N_u}}{w} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mu}{2Rt}}\ u^2du$$

$du = fu_{avg}$

$$= 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{Mu^2}{2RT}}\ u^3$$

$$U = 8\ \frac{RT}{\pi M}$$

∴ fraction

$$= 4\pi \times \left(\frac{M}{2\pi RT}\right)^{3/2} e^{-\frac{M}{2RT}\times\frac{8}{\pi}} \left(\frac{8RT}{\pi M}\right)^{3/2} \times 1$$

$$\text{Frac} = 4\pi \times \frac{1}{(2\pi)^{3/2}}\left(\frac{8}{\pi}\right)^{3/2} \times e^{-4/\pi}$$

$$\text{Frac} = \frac{4\pi\times(4)^{3/2}}{\pi^{3/2}} \times e^{-4/\pi}\ f$$

Fraction is independent of nature or state of gas is du = fu in range of μ

If p = 2.5,

$1 \times 60 = 2.5 \times (60 - x)$

$\therefore x = 36$ cm

As piston passes the cylinder will value 3

$V = 821 \times 20$

$P = 2.5$

$$\frac{2.5\times821\times20}{n_f} = \frac{1\times821\times60}{2}$$

$$n_f = \frac{2.5\times2\times20}{60}$$

$$\Rightarrow n_f = \frac{5}{3}$$

At x = 49,

$$P = \frac{60\times1}{15} = 4 < 4.4$$

Valve 4 does not open

At x = 50,

$$P = \frac{60}{10} = 6 > 4.8,\ \therefore \text{valve open}$$

But as it reaches x = 10, P = 4.8,

$$\frac{4.8\times10}{n_f} = \frac{1\times60}{2}$$

$$\therefore n_f = \frac{2\times48}{60} = \frac{8}{5}$$

Sol 15: (B, C) $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}}$

b) $\sqrt{\frac{M_{CO}}{M_{He}}} = \sqrt{\frac{28}{4}} = \sqrt{7} = 2.65$

(c) $\sqrt{\frac{M_{CO_2}}{M_{He}}} = \sqrt{\frac{44}{4}} = \sqrt{11}$

d) $\sqrt{\frac{M_{SO_2}}{M_{He}}} = \sqrt{\frac{64}{4}} = 4$

$\therefore$ B, D

Sol 16: (B, C) Boyles' law

Temperature is constant

$P \propto \frac{1}{V}$ or PV = constant

Which is clear from graph B & C

Where PV is constant

Sol 17: (B, D) Molar gas constant

$[R] = \left[\frac{PV}{nRT}\right]$ = pascal n^3 mole^{-1} K^{-1} = pascal m^3 = J

[R] = J mol^{-1} K^{-1}

$1J = \frac{1}{4.18}$ cal

R = 8.314 J mol^{-1} K^{-1}

$R = 8.314\left(\frac{1}{4.18}\right)$ cal mol^{-1} K^{-1}

= 1.987 cal mol^{-1} K^{-1}

R = 8.314 pascal m^3 mol^{-1} K^{-1}

$= 8.314\ \frac{\text{bar}}{10^5}\ 10^3$ dm^3 mol^{-1} K^{-1}

R = 0.08314 dm^3 bar mol^{-1} K^{-1}

Answer B, D

Sol 18: (A, B) Gas expands at constant T

V↑

PV = nRT

or PV = k

V↑ P↓

$K.E. = \frac{3}{2}RT$ = constant

A, B

Sol 19: (A, B, C, D) (a) a corrects the pressure term which is affected by attraction between molecules.

(b) (V – nb) $\therefore$ b corrects the volume and excludes the volume occupied by molecules itself

(c) $[P] = \left[\frac{an^2}{V^2}\right] \Rightarrow [a] = \left[\frac{PV^2}{n^2}\right]$

$\Rightarrow$ atm L^2 mol^{-2}

(d) $[V] = [nb] \Rightarrow [b] = \left[\frac{V}{n}\right]$

$\Rightarrow$ L mol^{-1}

Assertion Reasoning Type

Sol 20: (E) Assertion is wrong as co-volume = b

$b = 4\pi R^3 \rightarrow$ Dependent on size of particle reason is true

Sol 21: (D) Both are false

P vs $\frac{1}{V}$ is not always a straight line

$P = \frac{nRT}{V}$ (temp may vary)

$P \propto V$ (X)

Sol 22: (A) Factual

Sol 23: (C) Rate of diffusion $\propto \frac{1}{\sqrt{\mu}}$

$\therefore$ Assertion is correct

The reason is false

As K.E. = $\frac{3}{2}$ RT, independent of mass

Sol 24: (A) CH_4, CO_2 has value of Z < 1

Reason: Z < 1 due to repulsive forces

Comprehension Type

Paragraph 1:

Sol 25: (B) $Pe^{v/2} = nCT$

At V = 0, P = 1 of 500 K

At 2 moles of gas

$\Rightarrow 1 \times 1 = 2 \times 500 \times C$

$\Rightarrow \frac{1}{1000} = 10^{-3}$

Sol 26: (D) V = 2 litre, n = 2 mole

$\Rightarrow P \times e^{2/2} = n \times 0.001 \times T$

$\Rightarrow \frac{P}{T}$ = slope

$= \frac{0.002}{e} = \frac{2}{1000e}$

Sol 27: (A) V = 200 ℓ of O_2 at 1 at 200 K

Ideal gas

PV = nRT

$1 \times 200 = 0.0821 \times 200 \times n$

$n = \frac{1}{0.0821}$

$P \times e^{\frac{200}{2}} = \frac{1}{0.0821} \times 821 \times \frac{1}{1000}$

$P \times e^{100} = \frac{821}{82.1}$

$P = \frac{10}{e^{100}}$

Paragraph 2:

Sol 28: (A) $2(A)\,g \xrightarrow{\quad} 3B(g) + C(g)$

For a closed container,

Slope P – T curve

$= \frac{nR}{V}$ as V is constant

Slope $\propto$ n

If a is the degree of dissociation of A

$2A \xrightarrow{\quad} 3\,B + C$

Then $n_A - a \rightarrow \frac{3\alpha}{2} \qquad \frac{\alpha}{2}$

Total moles = $n_A - a + \frac{3\alpha}{2} + \frac{\alpha}{2} = n_A + \alpha$

$\therefore$ Slope $\propto n_A + \alpha$

Hence as slope ↑ es, $\propto$ ↑ es

$\therefore \alpha$ is lowest in $T_0 - T_1$ range

Sol 29: (C) If n_A = 1 mole, V = 0.0821,

R = 0.0821

$\Rightarrow$ PV = nRT

$\therefore$ Slope = n = 1 + α

$\therefore \alpha_{T_0-T_1} = \tan 50^\circ - 1 = 1.19 - 1 = 0.19$

$\alpha_{T_1-T_2} = 1.42 - 1 = 0.42$

Match the Columns

Sol 30: A → s; B → r, C → q; D → p

(A) PV = nRT

n and T are constant

⇒ PV = constant

PV = C

$P^2 = C\,\dfrac{P}{V}$

$x^2 = cy$

A represent parabolic curve, $x^2 = cy$ passing through origin

$A \xrightarrow{\quad} s$

(B) PV = nRT

Graph similar to $\dfrac{1}{x^2}$

$\dfrac{P}{V}\,V^2 = C$

$B \xrightarrow{\quad} r$

$yx^2 = C$

$y = \dfrac{c}{x^2} \quad P^{-2} = x$

(C) $\dfrac{V}{P}$ Vs $P^2 \quad \dfrac{PV}{PV^2} = \dfrac{\text{Constant}}{P^2}$

y = x constant   same as x

$C \xrightarrow{\quad} q$

(D) $\dfrac{P}{V}$ v/s log P

PV = constant

$P^2 = \text{constant}\ \dfrac{P}{V}$

Log P = x $D \xrightarrow{\quad} p$

⇒ P = ex

$e^x = y$ constant $\xrightarrow{\quad}$ similar to exponential function.

Sol 31: A → r; B → s, C → p; D → q

(A) $\dfrac{1}{V^2}$ Vs P

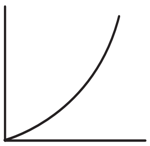
$PV = k; \Rightarrow P = \dfrac{k}{V}$

$\Rightarrow P = k\sqrt{\dfrac{1}{V^2}}$

$P \to x\ \dfrac{1}{V^2} \to y$

$\Rightarrow x = k\sqrt{y}$

$y = \dfrac{x^2}{k}$



(R)

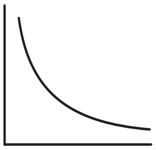
(B) V = kT   V Vs $\dfrac{1}{T}$

V = y

$\dfrac{1}{T} = x \Rightarrow T = \dfrac{1}{x}$

$y = \dfrac{k}{x}$

xy = k



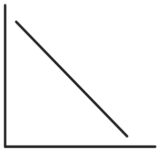
(S)

(C) log P Vs log V

PV = k

Log P + log V = log k

y x = log k



(P)

(D) V Vs $\dfrac{1}{P^2}$

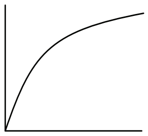
PV = k

$V = y, \quad \dfrac{1}{P^2} = x$

$P = \dfrac{1}{\sqrt{x}}$

$\dfrac{1}{\sqrt{x}}\ y = k$

$y = \sqrt{x}$



(Q)

Previous Years' Questions

Sol 1: (A) The two types of speeds are defined as; Roots mean square speed $(u_{rms}) = \sqrt{\dfrac{3RT}{M}}$

Average speed $(u_{avg}) = \sqrt{\dfrac{8RT}{\pi M}}$

For the same gas, at a given temperature, M and T are same therefore

$$\frac{\mu_{rms}}{u_{avg}} = \sqrt{\frac{3RT}{M}} : \sqrt{\frac{8RT}{\mu M}}$$

$$= \sqrt{3} : \sqrt{\frac{8}{\pi}}$$

$$= \sqrt{3} : \sqrt{2.54}$$

$$= 1.085 : 1$$

Sol 2: (A) If x g of both oxygen and methane are mixed then :

Mole of oxygen = $\frac{x}{32}$

Mole of methane = $\frac{x}{16}$

$\Rightarrow$ Mole fraction of oxygen = $\dfrac{\frac{x}{32}}{\frac{x}{32}+\frac{x}{16}} = \frac{1}{3}$

According to law of partial pressure

Partial pressure of oxygen (p_{o_2})

= Mole-fraction x total pressure

$$\Rightarrow \frac{p_{O_2}}{P} = \frac{1}{3}$$

Sol 3: (B) According to kinetic theory, average kinetic energy ($\in$) = $\frac{3}{2}$ K_BT

Where, k_B is Boltzmann's constant. Since, it is independent of molar mass, it will be same for He and H_2 at a given temperature.

Sol 4: (C) The ease of liquification of a gas depends on their intermolecular force of attraction which in turn is measured in terms of van der Waals' constant 'a'. Hence, higher the value of 'a', greater the intermolecular force of attraction, easier the liquification. In the present case, NH_3 has highest 'a', can most easily be liquefied.

Sol 5: (C) At high temperature and low pressure, the gas volume is infinitely large and both intermolecular force as well as molecular volume can be ignored. Under this condition postulates of kinetic theory applies appropriately and gas approaches ideal behaviour.

Sol 6: (C) Root mean square speed $U_{rms} = \sqrt{\frac{3RT}{M}}$

$$\Rightarrow \frac{u_{rms}(H_2)}{u_{rms}(N_2)} = \sqrt{7} = \sqrt{\frac{T(H_2)}{2} \times \frac{28}{T(N_2)}}$$

$$\Rightarrow 7 = \frac{14T(H_2)}{T(N_2)}$$

$\Rightarrow$ $T(N_2) = 2T(H_2)$, ie, $T(H_2) < T(N_2)$

Sol 7: (C) Let us consider, 1.0 L of liquid water is converted into steam Volume of H_2O (l) = 1L, mass = 1000 g

$\Rightarrow$ Volume of 1000 g steam = $\frac{1000}{0.0006}$ cm^3

$\because$ Volume of molecules in $\frac{1000}{0.0006}$ cm^3 steam = 1000 cm^3

$\therefore$ Volume of molecules in

1000 cm^3 steam = $\frac{1000}{1000} \times 0.0006 \times 1000 = 0.60$ cm^3

Sol 8: (B) In the van der Waals' equation :

$$\left(p + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

The additional factor in pressure, ie, $\frac{n^2a}{V^2}$ corrects for intermolecular force while 'b' corrects for molecular volume.

Sol 9: (A, B) Pressure is inversely proportional to volume at constant temperature, hence (A) is correct.

Average kinetic energy of a gas is directly proportional to absolute temperature, hence (B) is correct.

Expansion at constant temperature cannot change the number of molecules, hence (D) is incorrect.

Sol 10: (A, C) (A) is correct because in the limit of large volume, both intermolecular force and molecular volume becomes negligible in comparison to volume of gas.

(B) is wrong statement because in the limit of large pressure Z > 1

(C) is correct statement. For a van der Waals' gas, van der Waals constants 'a' and 'b' are characteristic of a gas, independent of temperature.

(D) is wrong statement because 'Z' can be either less or greater than unity, hence real pressure can be less or greater than ideal pressure.

Sol 11: (A, C, D) (A) According to a postulate of kinetic theory of gases, collision between the molecules as well as with the wall of container is perfectly clastic in nature.

(B) If a gas molecule of man 'm' moving with speed 'u' collide to the wall of container, the change in momentum is $\Delta_p = -2mu$. Therefore, heavier molecule will transfer more momentum to the wall as there will be greater change in momentum of the colliding gas molecule. However this is not postulated in kinetic theory.

(C) According to Maxwell-Boltzmann distribution of molecular speed, very few molecules have either very high or very low speeds. Most of the molecules moves in a specific, intermediate speed range.

(D) According to kinetic theory of gases, a gas molecule moves in straight line unless it collide with another molecule or to the wall of container and change in momentum is observed only after collision.

Sol 12: (A) 'a' is the measure of intermolecular force of attraction. Greater the intermolecular force of attraction (H– bond in the present case) higher the value of 'a'.

Sol 13: (D) Assertion is wrong because besides amount, pressure also depends on volume. However reason is correct because both frequency of collisions and impact are directly proportional to root mean square speed with is proportional to square-root of absolute temperature.

Sol 14: A → p, s; B → r, C → p, q; D → r

(A) At p = 200 atm, very high pressure, Z > 1 also, at such a high pressure, the pressure correction factor $\left(\frac{n^2a}{V^2}\right)$ can be ignored is comparison to p.

(B) At P ~ 0, gas will behave like an ideal gas, pV = nRT.

(C) CO_2 (p = 1 atm, T = 273 K), Z < 1.

(D) At very large molar volume, real gas behaves like an ideal gas.

Sol 15: Since, the external pressure is 1.0 atm, the gas pressure is also 1.0 atm as piston is movable. Out of this 1.0 atm partial pressure due to unknown compound is 0.68 atm.

Therefore, partial pressure of He

= 1.00 – 0.68

= 0.32 atm.

$$\Rightarrow \text{Volume} = \frac{n(\text{He})RT}{p(\text{He})} = \frac{0.1 \times 0.082 \times 273}{0.32} = 7\text{ L.}$$

⇒ Volume of container = Volume of He.

Sol 16: The total moles gaseous mixture

$$= \frac{pV}{RT} = \frac{1 \times 40}{0.082 \times 400}$$

Let the mixture contain x mole of ethane.

Therefore,

$$C_2H_6 + \frac{7}{2}O_2 \to 2CO_2 + 3H_2O$$

$$C_2H_4 + 3O_2 \to 2CO_2 + 2H_2O$$

`1.22 – x

Total moles of O_2 required

$$= \frac{7}{2}x + 3(1.22 - x)$$

$$= \frac{x}{2} + 3.66$$

$$\Rightarrow \frac{130}{32} = \frac{x}{2} + 3.66$$

⇒ x = 0.805 mole ethane and 0.415 mole ethane.

$$\Rightarrow \text{Mole fraction of ethane} = \frac{0.805}{1.22} = 0.66$$

Mole fraction of ethane = 1–0.66 = 0.34

Sol 17: In case of negligible molecular volume, b = 0, For 1 mole of gas

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

$$\Rightarrow pV + \frac{a}{V} = RT$$

$$\Rightarrow \frac{pV}{RT} + \frac{a}{VRT}$$

$$\left[\because \frac{pV}{RT} = 2\right] = 1$$

$$\Rightarrow Z + \frac{a}{\left(\frac{ZRT}{p}\right)RT} = 1$$

$$Z + \frac{ap}{ZR^2T^2} = 1$$

$$\Rightarrow a = \frac{ZR^2T^2(1-Z)}{p}$$

$$= \frac{0.5(0.082 \times 273)^2(1-0.5)}{100}$$

$a = 1.25$ atm $L^2\ mol^{-2}$

Sol 18:(D) Given, $u_{rms} = u_{rms}$

$$\Rightarrow \sqrt{\frac{3RT}{M(X)}} = \sqrt{\frac{2RT}{M(Y)}}$$

$$\Rightarrow \frac{3R \times 400}{40} = \frac{2R \times 60}{M(Y)}$$

$\Rightarrow M(Y) = 4.$

Sol 19: A → p, s; B → r; C → p, q; D → p, s

(A) $Z = \frac{PV_m}{RT}$ at high pressure and low temperature.

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

(B) For hydrogen gas value of Z = 1 at P = 0 and it increase continuously on increasing pressure.

(C) CO_2 molecules have larger attractive forces, under normal conditions.

(D) $Z = \frac{PV_m}{RT}$, at very large molar volume $Z \neq 1$.

Sol 20: (A, C, D) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

At low pressure, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly.

a and b are characteristic of a gas and are independent of temperature. The term $\left(P + \frac{an^2}{V^2}\right)$ represents the pressure exerted by an ideal gas while P represents the pressure exerted by a real gas.

Sol 21: (C) At large inter-ionic distances (because a → 0) the P.E. would remain constant. However, when r → 0; repulsion would suddenly increase.

Sol 22: (D) Diffusion coefficient ∝ mean free path × mean speed

$$D_1 \propto \lambda_1 C_1$$

$$C_2 = 2C_1$$

$$\lambda_2 = \frac{\lambda_1}{2} \times 4 = 2\lambda_1$$

$$D_2 \propto \lambda_2 C_2$$

$$\frac{D_2}{D_1} = \frac{\lambda_2 C_2}{\lambda_1 C_1} = 4$$