

THE GAS LAWS

Various gas laws were given from time to time to explain the behaviour of gases.

1. Boyle's law : The volume of given mass of a gas is inversely proportional to pressure at constant temperature.

$$V \propto \frac{1}{P} \quad (\text{at constant mass and } T)$$

or $PV = \text{constant} \quad \dots(1)$

2. Charles' law : The volume of given mass of a gas is directly proportional to absolute temperature at constant pressure.

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

or $\frac{V}{T} = \text{constant} \quad \dots(2)$
(Gay-Lussac's law)

3. Pressure-temperature law : The pressure of a given mass of a gas is directly proportional to temperature at constant volume.

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

or $\frac{P}{T} = \text{constant} \quad \dots(3)$

4. The Gas equation :

$$PV = RT \quad (\text{for one mole gas}) \quad \dots(4)$$

and $PV = nRT \quad (\text{for } n \text{ mole gas}) \quad \dots(5)$

$$\therefore PV = \frac{w}{M} RT \quad \left(\because n = \frac{w}{M} \right) \quad \dots(6)$$

where, R is molar gas constant, w is mass of gas and M is molar mass of gas.

5. Physical significance of R and its values in different units:

For 1 mole of an ideal gas

$$R = \frac{PV}{T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}}$$

$$= \frac{(\text{Force} / \text{Area}) \times (\text{Area} \times \text{Length})}{\text{Temperature}} = \frac{\text{Force} \times \text{Length}}{\text{Temperature}}$$

Thus, R represents work done per degree per mol. The values of R may be calculated in different units.

Since, 1 mole of any gas at NTP (273 K and 1 atm) occupies 22.4 litre.

$$R = \frac{1 \times 22.4}{273} = 0.0821 \text{ lit-atm per degree per mol}$$

To calculate R in CGS unit,

$$n = 1 \text{ mole,}$$

$$P = 1 \text{ atm} = 76 \text{ cm}$$

$$\text{Hg} = 76 \times 13.6 \times 981 \text{ dyne/cm}^2$$

$$V = 22400 \text{ cc, } T = 273 \text{ K}$$

$$R = \frac{76 \times 13.6 \times 981 \times 22400}{273}$$

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

NOTE : (i) While solving the numericals one should keep in mind proper units.

	Litre atmosphere	CGS	MKS
P	atm	dyne cm ⁻²	Nm ⁻² or Pa
V	litre	cm ³ or mL	m ³
w	g	g	kg
M	g	g	kg
R	0.821 litre-atm K ⁻¹ mol ⁻¹	$8.314 \times 10^7 \text{ erg K}^{-1} \text{mol}^{-1}$	$8.314 \text{ J K}^{-1} \text{mol}^{-1}$
T	Kelvin	Kelvin	Kelvin

The other values of $R = 2 \text{ calorie K}^{-1} \text{ mol}^{-1}$

$$= 2 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}$$

$$= 5.18976 \times 10^{19} \text{ eV K}^{-1} \text{ mol}^{-1}$$

$$= 8.314 \text{ m}^3 \text{Pa K}^{-1} \text{mol}^{-1} \text{ or kPa dm}^3 \text{K}^{-1} \text{mol}^{-1}$$

$$= 82.06 \text{ atm cm}^3 \text{K}^{-1} \text{mol}^{-1}$$

$$= 62.36 \text{ litre torr K}^{-1} \text{mol}^{-1}$$

$$= 2783 \text{ foot poundal K}^{-1} \text{mol}^{-1}$$

(ii) Standard ambient temperature and pressure (SATP) represents $P = 1 \text{ bar} = 0.987 \text{ atm} = 10^5 \text{ Pa}$ and $T = 25^\circ \text{C}$.

(iii) Volume of 1 mole gas at 1 bar and 0°C is 22.71 litre.

(iv) Volume of 1 mole gas at STP.

(v) Volume of 1 mole gas at SATP is 24.79 litre.

- (vi) Isothermal compressibility constant for an ideal gas,

$$\beta' = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{n, T} = \frac{1}{P}$$

- (vii) Thermal expansion coefficient of an ideal gas,

$$\alpha' = \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{P, n} = \frac{1}{T}$$

6. NTP or STP : NTP is referred as normal temperature and pressure.

STP is referred as standard temperature and pressure.

Both represent the state when

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

$$= 101325 \text{ Pascal} = 0.987 \text{ bar}$$

$$T = 0^\circ \text{C} = 273.14 \text{ K} \approx 273 \text{ K}$$

7. Dalton's law of partial pressure : The pressure exerted by a gaseous mixture (P_M) is equal to the sum of partial pressure of each component present in mixture, i.e.,

$$P_M = P'_A + P'_B + P'_C + \dots \quad \dots(7)$$

where, $P'_A, P'_B, \dots$ are partial pressures of each component in the mixture, defined as the pressure which it would exert if same amount is filled alone in the same container at same temperature. **The law is valid only for gases which do not combine with each other under normal conditions.**

Let n_A mole of A , n_B mole of B ... be filled in a container of volume V at temperature T , then

$$P_M = (n_A + n_B + n_C + \dots) \frac{RT}{V} \quad \dots(8)$$

$$\text{Also, } P'_A = n_A \frac{RT}{V} \quad \dots(9)$$

$$\therefore \frac{P'_A}{P_M} = \frac{n_A}{n_A + n_B + n_C + \dots} \quad \dots(10)$$

$$\text{or } P'_A = P_M \times \text{mole fraction of } A \text{ in mixture}$$

$$\text{or } P' = P_M \times \text{mole fraction of component in mixture} \quad \dots(11)$$

NOTE : 1. Saturated vapours do not obey gas laws except Dalton's law of partial pressure, i.e.,

$$\begin{aligned} P_{\text{moist gas}} &= P_{\text{dry gas}} + P_{\text{water vapour}} \\ P_{\text{dry gas}} &= P_{\text{moist gas}} - P_{\text{water vapour}} \\ &= P_{\text{moist gas}} - \text{aqueous tension} \end{aligned}$$

2. Aqueous tension remains constant at constant temperature.

3. Relative humidity

$$= \frac{\text{Mass of } \text{H}_2\text{O}_{(v)} \text{ in air}}{\text{Mass of } \text{H}_2\text{O}_{(v)} \text{ required to saturate air}}$$

8. Graham's law of diffusion : The rate of diffusion (r) of a gas at constant temperature is directly proportional to its pressure as well as inversely proportional to square root of its vapour density or molar mass.

$$\therefore r \propto P \quad \text{and} \quad r \propto \frac{1}{\sqrt{M}}$$

$$\text{or } r \propto \frac{P}{\sqrt{M}} \quad (\text{at constant temperature})$$

$$\text{For gas I} \quad r_1 \propto \frac{P_1}{\sqrt{M_1}}$$

$$\text{For gas II} \quad r_2 \propto \frac{P_2}{\sqrt{M_2}}$$

$$\therefore \frac{r_1}{r_2} = \frac{P_1}{P_2} \times \sqrt{\frac{M_2}{M_1}} \quad (\text{at constant } T) \quad \dots(12)$$

If pressure is also constant

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{d_2}{d_1}} \quad (\text{at constant } P \text{ and } T) \quad \dots(13)$$

where, d_1, d_2 are vapour densities of gases and

$$\text{V.D.} = \frac{\text{molar mass}}{2}$$

The rate of diffusion r may also be expressed as

$$r = \frac{V}{t} \quad \text{where } V \text{ volume of gas diffuses in time } t$$

$$r = \frac{n}{t} \quad \text{where } n \text{ mole of gas diffuses in time } t$$

$$r = \frac{d}{t} \quad \text{where } d \text{ distance is travelled by gas molecules in time } t$$

$\therefore$ By Eq. (12) at constant T By Eq. (13) at constant P and T

$$\frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \quad \frac{V_1}{t_1} \times \frac{t_2}{V_2} = \sqrt{\frac{M_2}{M_1}} \quad \dots(14)$$

$$\frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \quad \frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \quad \dots(15)$$

$$\frac{d_1}{t_1} \times \frac{t_2}{d_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2} \quad \frac{d_1}{t_1} \times \frac{t_2}{d_2} = \sqrt{\frac{M_2}{M_1}} \quad \dots(16)$$

Also, in terms of mass of gas diffused, Eq. (15) may be written as

$$\therefore \frac{w_1}{M_1 t_1} \times \frac{M_2 t_2}{w_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\therefore \frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{M_1}{M_2}$$

$$\text{or } \frac{w_1}{t_1} \times \frac{t_2}{w_2} = \sqrt{\frac{M_1}{M_2}} \quad \dots(17)$$

If a mixture of heavier gas B and a lighter gas A is placed in contact with a porous barrier, the gas passing through will be enriched in lighter component by a factor $\sqrt{\frac{M_B}{M_A}}$, called

enrichment factor because lighter molecules effuse more rapidly than heavier one. The remaining gas will be enriched in the heavier component. Each passage gives an enrichment factor equal to $\sqrt{\frac{M_B}{M_A}}$ and so thousands of such barriers in succession are necessary to provide sufficient enrichment of heavier component.

Thus, enrichment factor for first barrier or operation
 $f_1 = \sqrt{\frac{M_B}{M_A}}$

∴ Overall separation or enrichment factor $f = \frac{n'_A/n'_B}{n_A/n_B}$

where, n_A , n_B and n'_A , n'_B are the concentrations of two isotopically different components before and after processing. If the required enrichment of gas A is attained in x -operations then,

$$(f_1)^x = \frac{n'_A/n'_B}{n_A/n_B} = f$$

or $x \log f_1 = \log \left[\frac{n'_A/n'_B}{n_A/n_B} \right]$

or $x \log \left[\frac{M_B}{M_A} \right]^{1/2} = \log \left[\frac{n'_A/n'_B}{n_A/n_B} \right]$

or $\frac{x}{2} \log \left[\frac{M_B}{M_A} \right] = \log \left[\frac{n'_A/n'_B}{n_A/n_B} \right]$

or $x = \frac{2 \log \left(\frac{n'_A/n'_B}{n_A/n_B} \right)}{\log \left(\frac{M_B}{M_A} \right)} = \frac{2 \log f}{\log \left(\frac{M_B}{M_A} \right)} \quad \dots(18)$

Note : 1. Instantaneous rate of diffusion, $-\frac{dP}{dt} \propto \frac{P}{\sqrt{M}}$.

On integration under limits P_1 to P_2 and from 0 to t , we get

$$P_2 = P_1 \cdot e^{-\frac{Kt}{\sqrt{M}}}$$

2. Rate of diffusion, $\frac{\partial V}{\partial t}$ at constant P and T , through a pin hole of area A

$$\frac{\partial V}{\partial t} = \frac{A}{3} \sqrt{\frac{2}{\pi}} \cdot u_{rms}$$

9. The kinetic equation : For a gas,

$$PV = \frac{1}{3} m n u_{rms}^2 \quad \dots(19)$$

where, P is its pressure, V is its volume, m is mass of one molecule, n is no. of molecules of gas

u_{rms} is root mean square speed

$$= \sqrt{\left(\frac{u_1^2 + u_2^2 + u_3^2 + \dots}{n} \right)} = \sqrt{\frac{\sum u^2}{n}} \quad \dots(20)$$

Also, if n_1 molecules are moving with speed u_1 , n_2 molecules with speed u_2 and so on, then,

$$u_{rms} = \sqrt{\frac{n_1 u_1^2 + n_2 u_2^2 + n_3 u_3^2 + \dots}{n_1 + n_2 + n_3}} = \sqrt{\frac{\sum n u^2}{\sum n}} \quad \dots(21)$$

If there is 1 mole of gas then $m \times N = \text{molar mass}$
 $(\because n = N = \text{Av. No.})$

$$\therefore PV = \frac{1}{3} M u_{rms}^2 \quad \text{or} \quad u_{rms}^2 = \frac{3PV}{M}$$

$$\text{or} \quad u = \sqrt{\left(\frac{3PV}{M} \right)} = \sqrt{\left(\frac{3RT}{M} \right)} = \sqrt{\left(\frac{3P}{d} \right)} \quad \dots(22)$$

$(\because \frac{M}{V} = \text{density})$

NOTE : While calculating u one should keep in mind,

(a) The proper units of terms

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

If temperature is mentioned, always use $u = \sqrt{\left(\frac{3RT}{M} \right)}$, since, u_{rms} depends only on temperature and is independent of P , V and d .

$$\text{Average speed, } u_{AV} = \frac{u_1 + u_2 + u_3 + \dots}{n} \quad \dots(23)$$

$$\text{or} \quad u_{AV} = \frac{n_1 u_1 + n_2 u_2 + n_3 u_3 + \dots}{n_1 + n_2 + n_3} \quad \dots(24)$$

$$\text{Average speed, } u_{AV} = \sqrt{\left(\frac{8RT}{\pi M} \right)} \quad \dots(25)$$

$$\text{and most probable speed, } u_{MP} = \sqrt{\left(\frac{2RT}{M} \right)} \quad \dots(26)$$

$$\therefore u_{MP} : u_{AV} : u_{rms} :: 1 : \sqrt{\left(\frac{4}{\pi} \right)} : \sqrt{\left(\frac{3}{2} \right)}$$

$$u_{MP} : u_{AV} : u_{rms} :: 1 : 1.128 : 1.224 \quad \dots(27)$$

10. Kinetic energy : (for 1 mole gas)

$$PV = \frac{1}{3} M u_{rms}^2 = \frac{2}{3} \times \frac{1}{2} M u_{rms}^2 = \frac{2}{3} \times \text{KE/mol}$$

$$\therefore \text{Translational KE/mol} = \frac{3}{2} PV = \frac{3}{2} RT \quad \dots(28)$$

$$\therefore \text{Translational KE/molecule} = \frac{3}{2} \frac{R}{N} T = \frac{3}{2} kT \quad \dots(29)$$

$$\text{where, } k \text{ is Boltzmann's constant and } k = \frac{R}{N} \quad \dots(30)$$

$$\text{For } n \text{ mole of a gas, } KE = \frac{3}{2} nRT \quad \dots(31)$$

11. Mean free path : The distance travelled in between two successive collisions of a molecule is free path. The average of all such free paths is mean free path.

$$\therefore \text{Mean free path, } \lambda = \frac{d_1 + d_2 + \dots + d_n}{n} \quad \dots(32)$$

where, $d_1, d_2, \dots, d_n$ are free paths travelled by a molecule.

12. Collision frequency ($c.f.$) : No. of collisions taking place in unit time

$$c.f. = \frac{\text{No. of collisions}}{\text{Time}} = \frac{u_{rms}}{\lambda} \quad \dots(33)$$

13. Limitations of gas equation and van der Waals' equation for gases : Gases show deviations from ideal gas behaviour (i.e., $PV = RT$) preferably more at high P and low T . The deviations are expressed in terms of compressibility factor (Z) expressed as

$$Z = \frac{PV}{nRT} \quad (\text{for } n \text{ mole gas}) \quad \dots(34)$$

$$\text{or} \quad Z = \frac{PV}{RT} \quad (\text{for 1 mole gas}) \quad \dots(35)$$

NOTE : 1. $Z = 1$ for ideal gas.

2. $Z > 1$ means for positive deviation from ideal gas behaviour; usually at high P : $Z > 1$, which means $PV > RT$ and attractive forces predominate.

3. $Z < 1$ means negative deviation from ideal gas behaviour; usually at low P : $Z < 1$, which means $PV < RT$ and repulsive forces predominate.

4. $Z = 1$ for real gases at normal P .

5. $Z > 1$ for H_2 and He at all pressure.

van der Waals' pointed out another equation to express behaviour of gases as,

$$\left[P + \frac{a}{V^2} \right] [V - b] = RT \quad (\text{for 1 mole gas}) \quad \dots(36)$$

$$\left[P + \frac{n^2 a}{V^2} \right] [V - nb] = nRT \quad (\text{for } n \text{ mole gas}) \quad \dots(37)$$

where, a = van der Waals' constant for attraction

b = van der Waals' constant for volume

NOTE : (i) Since ' b ' is four times of the actual volume of gaseous molecules

$$\therefore b = 4N \times v = 4 \times \text{Avogadro's no.} \times \frac{4}{3}\pi r^3$$

where, r is radius of one gaseous molecule and v is volume of one molecule of gas in rest.

(ii) Units of a = atm litre² mol⁻² = atm dm³ mol⁻²

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

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

$$\text{Units of } b = \text{litre mol}^{-1} = \text{dm}^3 \text{ mol}^{-1}$$

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

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

14. Molar heat capacity of ideal gases : Specific heat c , of a substance is defined as the amount of heat required to raise the temperature of 1 g of substance through 1°C, the unit of specific heat is calorie g⁻¹ K⁻¹. (1 cal is defined as the amount of heat required to raise the temperature of 1 g of water through 1°C).

Molar heat capacity C , is defined as the amount of heat required to raise the temperature of 1 mole of a gas through 1°C. Thus,

$$\text{Molar heat capacity} = \text{Sp. heat} \times \text{Molar mass of the gas} \\ C_p = c_p \times M \quad \dots(38)$$

$$C_v = c_v \times M \quad \dots(39)$$

For gases there are two values of molar heats, i.e., molar heat at constant pressure and molar heat at constant volume respectively denoted by C_p and C_v . C_p is greater than C_v .

$$\text{and} \quad C_p - C_v = R \quad \dots(40)$$

$$c_p - c_v = \frac{R}{M} \quad \dots(41)$$

For a monoatomic gas $C_p = 5 \text{ cal}$ and $C_v = 3 \text{ cal}$

$$\text{Poisson's ratio } (\gamma): \quad \gamma = \frac{C_p}{C_v} \quad \dots(42)$$

$$\gamma = \frac{5}{3} = 1.67$$

For diatomic gas $C_p = 7 \text{ cal}$ and $C_v = 5 \text{ cal}$

$$\gamma = \frac{7}{5} = 1.40$$

For polyatomic gas $C_p = 8 \text{ cal}$ and $C_v = 6 \text{ cal}$

$$\gamma = \frac{8}{6} = 1.33$$

where, c_p and c_v are specific heats and M is molar mass.

15. Critical constants :

$$\text{Critical volume,} \quad V_c = 3b \quad \dots(43)$$

$$\text{Critical pressure,} \quad P_c = \frac{a}{27b^2} \quad \dots(44)$$

$$\text{Critical temperature,} \quad T_c = \frac{8a}{27Rb} \quad \dots(45)$$

Note : 1. Liquefaction of a gas is a continuous process.

2. Ideal gas can not be liquefied.

16. Boyle's temperature : The temperature range at which real gases obey gas laws is called Boyle's temperature (T_b)

$$T_b = \frac{a}{Rb} \quad \dots(46)$$

17. Inversion temperature : The temperature below which a gas on subjecting to Joule-Thomson effect shows cooling effect ($\mu_{J.T.} = +ve$) and above which it shows heating effect ($\mu_{J.T.} = -ve$) is called inversion temperature (T_i)

$$T_i = \frac{2a}{Rb} \quad \dots(47)$$

$\mu_{J.T.}$ is Joule-Thomson coefficient expressed as

$$\left(\frac{\partial T}{\partial P} \right)_H = \mu_{J.T.} \quad \dots(48)$$

$\mu_{J.T.} = 0$ for an ideal gas.

18. Equation for law of corresponding state :

$$\left[P_r + \frac{3}{V_r^2} \right] [3V_r - 1] = 8T_r \quad \dots(49)$$

where $P_r = \frac{P}{P_c}$; $V_r = \frac{V}{V_c}$ and $T_r = \frac{T}{T_c}$

Note : At corresponding state; $Z = \frac{3P_r \cdot V_r}{8T_r}$

● NUMERICAL PROBLEMS ●

1. A gas occupies 300 mL at 27°C and 730 mm pressure. What would be its volume at STP?
2. A gas at 0°C and 1 atm pressure occupies 2.5 litre. What change in temperature would be necessary if the pressure is to be adjusted to 1.5 atm and the gas has been transferred to a 2.0 litre container?
3. Calculate the volume occupied by 7 g N₂ at 27°C and 750 mm of Hg.
4. A container having 3 mole of gas occupies 60 litre at pressure P and T . If 0.01 mole of gas are introduced at same P and T , what will be the change in volume?
5. Calculate the mass of CH₄ in a 9 litre cylinder at 16 atm and 27°C. ($R = 0.08 \text{ L atm K}^{-1}$)
6. 3.7 g of a gas at 25°C occupy the same volume as 0.184 g H₂ at 17°C at same pressure. What is the molar mass of gas?
7. 5 g of ethane are confined in a bulb of 1 litre capacity. The bulb is so weak that it will burst if the pressure exceeds 10 atm. At what temperature will the pressure of gas reach the bursting value?
8. In Victor Meyer's experiment, 0.23 g of a volatile solute displaced air which measures 112 mL at NTP. Calculate the vapour density and molar mass of substance.
9. What should be the percentage increase in pressure for a 5% decrease in volume of a gas at constant temperature?
10. O₂ is present in one litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate no. of O₂ molecules at 0°C.
11. The pressure of the atmosphere is 2×10^{-6} mm at about 100 mile above the earth and temperature is -180°C. How many mole are there in 1 mL gas at this altitude?
12. A 1.5 litre sample of a gas having density 1.25 kg/m³ at 1.0 atm and 0°C was compressed to 575 atm resulting in a gas volume of 3.92 cm³ in violation of Boyle's law. What is the final density of this gas?
13. The pressure exerted by 12 g of an ideal gas at temperature $t^\circ\text{C}$ in a vessel of volume V litre is one atm. When the temperature is increased by 10 degree at the same volume, the pressure increases by 10%. Calculate the temperature t and volume V . (Molar mass of the gas = 120). (IIT 1999)
14. An iron cylinder contains helium at a pressure of 250 kPa at 300 K. The cylinder can withstand a pressure of 1×10^6 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.
15. A volume of 95 mL N₂O at 27°C is collected in a graduated tube over mercury, the level of Hg inside the tube being 60 mm above the outside mercury level when barometer reads 750 mm.
 - (a) Calculate the volume of the same mass at STP.
 - (b) What volume would the same mass of gas occupy at 40°C when the barometric pressure is 745 mm and the level of Hg inside the tube 25 mm below the outside level?
16. An LPG (liquefied petroleum gas) cylinder weighs 14.8 kg when empty, when full, it masses 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27°C, the mass of full cylinder is reduced to 23.2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions and the final pressure inside the cylinder. Assume LPG to be n -butane with normal boiling point of 0°C. (IIT 1994)
17. A balloon blown up with 1 mole of gas has a volume of 480 mL at 5°C. The balloon is filled to $(7/8)$ th of its maximum capacity. Suggest,
 - (a) Will the balloon burst at 30°C?
 - (b) The minimum temperature at which it will burst.
 - (c) The pressure of gas inside the balloon at 5°C.
 - (d) The pressure of gas when balloon bursts.
18. 0.553 g of a boron-hydrogen compound created a pressure of 0.658 atm in a bulb of 407 mL at 100°C. Analysis showed it to be 85.7% boron. Calculate its molecular formula.
19. 1.47 litre of a gas is collected over water at 30°C and 744 mm of Hg. If the gas weighs 1.98 g and vapour pressure of water at 30°C is 32 mm, what is the molar mass of gas?
20. Calculate the density of CO₂ at 100°C and 800 mm Hg pressure.
21. A mixture of CO and CO₂ is found to have a density of 1.50 g/litre at 30°C and 730 mm. What is composition of mixture?
22. A spherical balloon of 21 cm diameter is to be filled up with H₂ at NTP from a cylinder containing the gas at 20 atm at 27°C. The cylinder can hold 2.82 litre of water at NTP. Calculate the number of balloons that can be filled up.
23. A balloon of diameter 20 metre weighs 100 kg. Calculate its payload, if it is filled with He at 1.0 atm and 27°C. Density of air is 1.2 kg m^{-3} .
[$R = 0.082 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$] (Roorkee 1994)
24. The mass of 350 mL of a diatomic gas at 0°C and 2 atm is 1 g. Calculate the mass in g of one atom.
25. A flask is of a capacity of one litre. What volume of air will escape from the flask if it is heated from 27°C to 37°C? Assume pressure is constant.

26. A student forgot to add the reaction mixture to the round bottomed flask at 27°C but put it on the flame. After a lapse of time, he realised his mistake. Using a pyrometer he found that the temperature of the flask was 477°C . What fraction of air would have expelled out?
27. An open flask contains air at 27°C . Calculate the temperature at which it should be heated so that,
 - (a) $\frac{1}{3}$ rd of air measured at 27°C escapes out.
 - (b) $\frac{1}{3}$ rd of air measured at final temperature escapes out.
28. 20% N_2O_4 molecules are dissociated in a sample of gas at 27°C and 760 torr. Calculate the density of the equilibrium mixture. [Roorkee 1996]
29. Two flasks of equal volume connected by a narrow tube (of negligible volume) are at 27°C and contain 0.70 mole of H_2 at 0.5 atm. One of the flask is then immersed into a bath kept at 127°C , while the other remains at 27°C . Calculate the final pressure and the number of mole of H_2 in each flask.
30. A vessel contains 7.1g chlorine gas at pressure P and temperature T K. On heating the vessel to 30° higher temperature, 246 mL of chlorine at 1 atm and 27°C is taken out to maintain same pressure in vessel. Calculate:
 - (a) the original temperature,
 - (b) if the gas is not allowed to escape out, the pressure increases by 0.11 atm. Calculate the volume of vessel and initial pressure.
31. A car tyre has a volume of 10 litre when inflated. The tyre is inflated to a pressure of 3 atm at 17°C with air. Due to driving the temperature of tyre increases to 47°C .
 - (a) What would be the pressure at this temperature?
 - (b) How many litre of air measured at 47°C and pressure of 1 atm should be let out to restore the tyre to 3 atm at 47°C ?
32. A gas filled freely collapsible balloon is pushed from the surface level of lake to a depth of 100 meter. Calculate what per cent of its original volume, the balloon finally has. Assume ideal gas nature.
33. Two glass bulbs of equal volumes 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.
34. Two glass bulbs of internal volumes 0.5 and 0.2 litre respectively are connected by a narrow tube of negligible volume. The pressure of air in the vessel is 75 cm at 17°C . The smaller bulb is immersed in melting ice and the larger bulb in boiling water. Calculate final pressure in the bulbs neglecting the expansion of glass.
35. The volume of the average adult lung when expanded is about 6 litre at 98.4°F , if the pressure of oxygen in inhaled air is 168 mm of Hg, calculate the mass of O_2 required to occupy the lung at 98.4°F .
36. Two gas containers with volumes 0.1 L and 1 L respectively are connected by a tube of negligible volume and contains air at a pressure of 1000 mm of Hg at 0°C . If the temperature of smaller container is raised to 100°C , what volume of air measured at 0°C and 760 mm of Hg will pass from it to a larger container.
37. A 2 litre flask of N_2 at 20°C and 70 cm P is connected with a 3 litre of another flask of O_2 at the same temperature and 100 cm P . What will be the final pressure after the gases have thoroughly mixed at the same temperature as before? Also calculate the mole % of each gas in the resulting mixture. The volume of stop cock may be neglected.
38. 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 of gases. Given, $R = 0.082 \text{ litre} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. (Roorkee 1997)
39. Equal masses of CH_4 and O_2 are mixed in an empty container of one litre at 27°C . Calculate the:
 - (a) fraction of total pressure exerted by O_2 .
 - (b) total pressure if the masses of gases are 32 g each.
40. Two gases A and B having molar mass 60 and 45 respectively are enclosed in a vessel. The mass of A is 0.50 g and that of B is 0.2 g. The total pressure of the mixture is 750 mm. Calculate partial pressure of the two gases.
41. A 20 g chunk of dry ice is placed in an empty 0.75 litre wine bottle tightly closed. What would be the final pressure in the bottle after all CO_2 has been evaporated and temperature reaches to 25°C ?
42. A gaseous mixture of O_2 and N_2 are in the ratio of 1:4 by mass. Calculate their ratio of molecules.
43. 50 litre of dry N_2 is passed through 36 g H_2O at 27°C . After passage of gas, there is a loss of 1.20 g in water. Calculate vapour pressure of water.
44. O_2 is collected over water at 20°C . The pressure inside shown by the gas is 740 mm of Hg. What is the pressure due to O_2 alone if V.P. of H_2O is 18 mm at 20°C ?
45. The density of a mixture of O_2 and N_2 at NTP is 1.3 g litre^{-1} . Calculate partial pressure of O_2 .
46. An evacuated glass vessel weighs 50.0 g when empty, 148.0 g when filled with a liquid of density 0.98 g mL^{-1} and 50.5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molar mass of the gas. (IIT 1998)

47. A jar contains a gas and a few drops of water at T K. The pressure in the jar is 830 mm of Hg. The temperature of the jar is reduced by 1%. The vapour pressures of water at two temperatures are 30 and 25 mm of Hg. Calculate the new pressure in the jar.
48. 2 g of a gas A are introduced into an evacuated flask kept at 25°C . The pressure is found to be 1 atm. If 3 g of another gas B are added to the same flask, the total pressure becomes 1.5 atm. Assuming ideal gas behaviour, calculate :
- the ratio of molar masses of M_A and M_B .
 - the volume of the vessel, if A is O_2 .
49. A long rectangular box is filled with Cl_2 (at. mass 35.45) which is known to contain only Cl^{35} and Cl^{37} . If the box could be divided by a partition and the two types of chlorine molecules put into the two compartments respectively, calculate, where should the partition be made if the pressure on both sides is to be equal. Is this pressure the same as the original pressure?
50. A narrow tube of uniform base, closed at one end has some air entrapped by a small quantity of water. If the pressure of the atmosphere is 760 mm of Hg and vapour pressure of H_2O at 12°C and 35°C are 10.5 mm Hg and 42 mm Hg respectively and the length of the air column is 10 cm at 12°C , what will be its length at 35°C ?
51. Mercury diffusion pumps may be used in the laboratory to produce a high vacuum. Cold traps are generally placed between the pump and the system to be evacuated. These cause condensation of mercury vapours and prevent mercury from diffusing back into the system. The minimum pressure of mercury that can exist in the system is the vapour pressure of mercury at the temperature of cold trap. Calculate the number of mercury atom per unit volume in a cold trap at -120°C . The vapour pressure of mercury at this temperature is 10^{-16} torr.
52. Helium is contained at 30.2°C in the system as shown in the figure. The levelling bulb (L) can be raised so as to fill the lower bulb with mercury and force the gas into the upper part of the device. The volume of bulb (A) to the mark ' a ' is 100.5 cm^3 and the volume of bulb (B) between the marks ' a ' and ' b ' is 110 cm^3 . The pressure exerted by the He is measured by the difference between the mercury levels in the device and in the evacuated arm of the manometer when mercury level is at ' b ', the pressure is 20.14 mm of Hg. What is the mass of the helium in container?
53. A glass capillary tube sealed at both ends is 100 cm long. It lies horizontally with the middle 10 cm containing Hg. The two ends of the tube which are equal in length contain air at 27°C and pressure of 76 cm of Hg. The tube is kept in a horizontal position such that the air column at one end is at 0°C , the other end is maintained at 127°C . Calculate the length of the air column and its pressure which is at 0°C . Neglect the change in volume of Hg and glass.
54. 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 76 cm of Hg. By what distance will the column of Hg be displaced if the tube is held vertical? (Roorkee Phy. 1989)
55. A vertical cylinder closed at both ends, is divided into two parts by a frictionless piston, each part containing one mole of air. At temperature 300 K, the volume of upper part is 4 times than that of the lower part. At what temperature will the volume of upper part be three times than that of lower part?
56. A thin tube of uniform cross-section is sealed at both ends. It lies horizontally. The middle 5 cm containing Hg and the two equal ends containing air at the same pressure P_0 . When the tube is held at an angle 60° with the vertical, the length of the air column above and below the mercury are 46 and 44.5 cm respectively. Calculate the pressure P_0 in cm of Hg. (The temperature of the system is kept at 30°C) [IIT Phy. 1986]
57. An under water bubble with a radius of 0.5 cm at the bottom of tank, where the temperature is 5°C and pressure is 3 atm rises to the surface, where temperature is 25°C and pressure is 1 atm. What will be the radius of bubble when it reaches to surface?
58. A mixture of N_2 and water vapours is admitted to a flask which contains a solid drying agent. Immediately after admission, the pressure of the flask is 760 mm. After standing some hours, the pressure reached a steady value of 745 mm,
- Calculate the composition in mole % of original mixture.
 - If the experiment is done at 20°C and the drying agent increases in mass by 0.15 g, what is the volume of flask? (neglect volume occupied by drying agent)
59. A vessel of volume 5 litre contains 1.4 g of nitrogen at a temperature 1800 K. Find the pressure of the gas if 30% of its molecules are dissociated into atom at this temperature.
60. A vertical hollow cylinder of height 1.52 m is fitted with a movable piston of negligible mass and thickness. The lower half of the cylinder contains an ideal gas and the upper half is filled with mercury. The cylinder is initially at 300 K. When the temperature is raised half of the mercury comes out of the cylinder. Find the temperature assuming the thermal expansion of mercury to be negligible. (Roorkee Phy. 1993)
61. Two closed vessels of equal volumes contain air at 105 kPa and 300 K are connected through a narrow tube

of negligible volume. If one of the vessel is maintained at 300 K and other at 400 K, what will be the new pressure in vessel? Also calculate the ratio of number of mole in each vessel.

62. One litre flask contains air, water vapour and a small amount of liquid water at a pressure of 200 mm Hg. If this is connected to another one litre evacuated flask, what will be the final pressure of the gas mixture at equilibrium? Assume the temperature to be 50°C. Aqueous tension at 50°C = 93 mm Hg.
63. A closed vessel contains air, saturated water vapours and excess of water. The total pressure in the vessel is 760 mm Hg at 25°C. The temperature is raised to 100°C. Calculate the total pressure in vessel at 100°C. Aqueous tension of H₂O at 25°C and 100°C are 24 mm and 760 mm Hg.
64. Find out the mass of water vapour per litre of air at 300 K when relative humidity is 50%. The saturation vapour pressure at 300 K is 3.6 kPa.
65. Assume that dry air contains 79% N₂ and 21% O₂ by volume. Calculate the density of dry air and moist air at 25°C and 1 atmospheric pressure when relative humidity is 60%. The vapour pressure of water at 25°C is 23.76 mm.

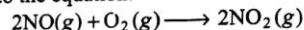
[Relative humidity is given by percentage relative humidity

$$= \frac{100 \times \text{partial pressure of water}}{\text{vapour pressure of water at that temperature}}]$$

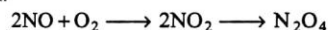
66. A mixture of H₂O, CO₂ and N₂ was trapped in a glass apparatus with a volume of 0.731 mL. The pressure of total mixture was 1.74 mm of Hg at 23°C. The sample was transferred to a bulb in contact with dry ice (-75°C) so that H₂O, are frozen out. When the sample returned to normal value of temperature, pressure was 1.32 mm of Hg. The sample was then transferred to a bulb in contact with liquid N₂ (-95°C) to freeze out CO₂. In the measured volume, pressure was 0.53 mm of Hg at original temperature. How many mole of each constituent are in mixture?
67. What would be the final pressure of O₂ in following experiment? A collapsed polyethylene bag of 30 litre capacity is partially blown up by the addition of 10 litre of N₂ at 0.965 atm at 298 K. Subsequently enough O₂ is pumped into bag so that at 298 K and external pressure of 0.990 atm, the bag contains full 30 litre.
68. A mixture of N₂, NO and NO₂ in a closed container was analysed by selective absorption of the oxides of nitrogen. The initial pressure was 3.0 cm. After treatment with water, which absorbs NO₂, the pressure left was 2.42 cm. A ferrous sulphate solution was then shaken with residual gas mixture to absorb NO after which the pressure was 1.24 cm. If vapour pressure of

H₂O, in gaseous mixture after shaking with H₂O and in FeSO₄ solution were 0.2 cm and 0.18 cm respectively calculate the mole % of gases in initial mixture. Assume all measurements are made at same *P* and *T*.

69. Calculate the change in pressure when 1.04 mole of NO and 20.0 g O₂ in a 20 litre vessel originally at 27°C react to produce the maximum quantity of NO₂ possible according to the equation.



70. A 40 mL of a mixture of H₂ and O₂ was placed in a gas burette at 18°C and 1 atm *P*. A spark was applied so that the formation of water was complete. The remaining pure gas had a volume of 10 mL at 18°C and 1 atm *P*. If the remaining gas was H₂, what was the initial mole % of H₂ in mixture?
71. A flask of capacity one litre containing NH₃ at 1 atm and 25°C. A spark is passed through until all the NH₃ is decomposed into N₂ and H₂. Calculate:
- the pressure of gases left at 25°C.
 - the mole of N₂ and H₂ formed.
72. At room temperature following reaction goes to completion:



Dimer N₂O₄ at 262 K is solid. A 250 mL flask and a 100 mL flask are separated by a stop cock. At 300 K, the nitric oxide in the larger flask exerts a pressure of 1.053 atm and the smaller one contains O₂ at 0.789 atm. The gases are mixed by opening the stop cock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of dimer, find out the pressure and composition of gas remaining at 220 K. (Assume gases behave ideally) (IIT 1992)

73. A compound exists in the gaseous phase both as monomer (*A*) and dimer (*A*₂). The molar mass of *A* is 48. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 litre and heated to Calculate the pressure developed if the compound exists as dimer to the extent of 50% by mass under these conditions.
74. 60 mL of a mixture of equal volumes of Cl₂ and an oxide of chlorine was heated and then cooled back to the original temperature. The resulting gas mixture was found to have volume of 75 mL. On treatment with caustic soda solution, the volume contracted to 15 mL. Assume that all measurements are made at the same *T* and *P*. Deduce the simplest formula for oxide of Cl₂. The oxide of Cl₂ on heating decomposes quantitatively to O₂ and Cl₂.
75. One litre of O₂ and one litre of H₂ are taken in a vessel of 2 litre capacity at NTP. The gases are made to combine to form water. Calculate:
- the mole and mass of water formed.

- (b) the amount of gas left in vessel.
 (c) the total pressure if the vessel is heated to 100°C .
 (d) mole of O_2 used for formation of water.
76. A space capsule is filled with neon at 1 atm and 290 K. The gas effuses through a pin hole into outer space at the rate that pressure drops by 0.3 torr/sec. If the capsule is filled with 30 mole % of He, 20 mole % of O_2 and 50 mole % of N_2 . What is the pressure drop under same condition?
77. 20 dm^3 of SO_2 diffuses through a porous partition in 60 second. What volume of O_2 will diffuse under similar conditions in 30 second? (Roorkee 1996)
78. Pure O_2 diffuses through an aperture in 224 second, whereas mixture of O_2 and another gas containing 80% O_2 diffuses from the same in 234 sec. What is molar mass of gas?
79. One mole of nitrogen gas at 0.8 atm takes 38 second to diffuse through a pinhole, whereas one mole of an unknown compound of xenon with fluorine at 1.6 atm takes 57 second to diffuse through the same hole. Calculate the molecular formula of the compound. (IIT 1999)
80. For 10 minute each, at 27°C , from two identical holes nitrogen and an unknown gas are leaked into a common vessel of 3 litre capacity. The resulting pressure is 4.18 bar and the mixture contains 0.4 mole of nitrogen. What is the molar mass of unknown gas?
81. The rates of diffusion of two gases A and B are in the ratio 1 : 4. If the ratio of their masses present in the mixture is 2 : 3, calculate the ratio of their mole fraction.
82. The composition of the equilibrium mixture ($\text{Cl}_2 \rightleftharpoons 2\text{Cl}$), which is attained at 1200°C , is determined by measuring the rate of effusion through a pinhole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms. (Atomic mass of Kr = 84) (IIT 1995)
83. A mixture containing 1.12 litre D_2 and 2.24 litre of H_2 at NTP is taken inside a bulb connected to another bulb through a stop cock with a small opening. The second bulb is fully evacuated. The stop cock is opened for a certain time and then closed. The first bulb is now found to contain 0.10 g of D_2 . Determine the % by mass of the gases in second bulb. (Roorkee 1998)
84. Calculate the relative rates of diffusion for $^{235}\text{UF}_6$ and $^{238}\text{UF}_6$ in gaseous form. Also if naturally occurring uranium ore having U^{235} and U^{238} in the ratio 0.72 and 99.28%, and if it is desired to enrich the U^{235} to 10% of the sample, making use of relative rates of diffusion of UF_6 having U^{235} and U^{238} isotopes, how many diffusion stages are required?
85. Naturally occurring hydrogen gas has abundance of $^1\text{H}^1\text{H}$ (molar mass 2) and $^1\text{H}^2\text{H}$ (molar mass 3). The % of $^1\text{H}^1\text{H} = 90.0\%$. In how much operations during diffusion of natural hydrogen gas will be enriched to 99.8% $^1\text{H}^1\text{H}$.
86. At 20°C , two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg of H_2 balloon leaks to a pressure of 1/2 atm in 1 hr. How long will it take for H_2 balloon to reach a pressure of 1/2 atm?
87. At 27°C , H_2 is leaked through a tiny hole into a vessel for 20 minute. Another unknown gas at the same T and P as that of H_2 is leaked through the same hole for 20 minute. After the effusion of the gases, the mixture exerts a pressure of 6 atm. The H_2 content of the mixture is 0.7 mole. If volume of container is 3 litre, what is molar mass of unknown gas? (IIT 1992)
88. A mixture of 0.5 mole of CO and 0.5 mole of CO_2 is taken in a vessel and allowed to effuse out through a pinhole into another vessel which has vacuum. If a total of A mole has effused out in time t, show that $M_1A + M_2(1-A) = 36$, where M_1 and M_2 are mean molar masses of the mixture that has effused out and the mixture still remaining in vessel respectively.
89. A straight glass tube has two inlets X and Y at the two ends of 200 cm long tube. HCl gas through inlet X and NH_3 gas through inlet Y are allowed to enter in the tube at the same time and same pressure. White fumes first appears at a point P inside the tube. Calculate distance of P from X.
90. At room temperature, NH_3 gas at 1 atm and HCl gas at P atm are allowed to effuse through identical pinholes from opposite ends of a glass tube of 1 metre 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 sent in. What is the value of P?
91. The pressure in bulb dropped from 2000 to 1500 mm of Hg in 47 minute when the contained O_2 leaked through a small hole. The bulb was then completely evacuated. A mixture of O_2 and another gas of molar mass 79 in the molar ratio 1 : 1 at a total pressure of 4000 mm of Hg was introduced. Find the mole ratio of two gases remaining in the bulb after a period of 74 minute.
92. A 4 : 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? (IIT 1994)
93. Calculate the root mean square speed and average speed for a sample of gas having 5, 10 and 15 molecules each one in a set is moving with a speed of 15×10^2 , 5×10^2 and $10 \times 10^2\text{ m s}^{-1}$ respectively.

94. Calculate root mean square speed, average speed and most probable speed of :
 (a) O_2 at STP.
 (b) Ethane at $27^\circ C$ and 720 mm of Hg.
 (c) O_2 at $17^\circ C$.
 (d) O_2 if its density is 0.0081 g mL^{-1} at 1 atm.
 (e) O_2 if 6.431 g of it occupies 5 litre at 750 mm.
 (f) O_3 at $20^\circ C$ and 82 cm Hg. (IIT 1985)
95. The average speed at T_1 K and the most probable speed at T_2 K of CO_2 gas is $9 \times 10^4 \text{ cm sec}^{-1}$. Calculate the value of T_1 and T_2 . (IIT 1990)
96. The average speed of an ideal gas molecule at $27^\circ C$ is 0.3 m sec^{-1} . Calculate average speed at $927^\circ C$.
97. Relate the three speeds with each other, i.e., u_{rms} , u_{AV} and u_{MP} .
98. The average velocity of gas molecules is 400 m/sec. Calculate its rms velocity at the same temperature. (IIT 2003)
99. The mass of molecule A is twice the mass of molecule B . The rms speed of A is twice the rms 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 in separate containers of equal volume?
100. Under 3 atm, 12.5 litre of a certain gas weigh 15 g, calculate the average speed of gaseous molecules.
101. Calculate the pressure exerted by 10^{23} gas molecules, each of mass 10^{-22} g in a container of volume one litre. The rms speed is 10^5 cm sec^{-1} .
102. Calculate the root mean square speed, total and average translational kinetic energy in joule of the molecules in 8 g methane at $27^\circ C$.
103. The mean kinetic energy of a molecule at $0^\circ C$ is $5.621 \times 10^{-14} \text{ erg}$. Calculate Boltzmann's constant. If the value of $R = 8.314 \times 10^7 \text{ erg}$, then also calculate the no. of molecules present in one mole of gas.
104. A glass bulb of 1 litre capacity contains 2×10^{21} molecules of nitrogen exerting pressure of $7.57 \times 10^3 \text{ Nm}^{-2}$. Calculate the root mean square speed and the temperature of gas molecules. If the ratio of u_{MP} to u_{rms} is 0.82, calculate u_{MP} for these molecules at this temperature. (IIT 1993)
105. Two bulbs A and B of equal capacity are filled with He and SO_2 respectively, at the same temperature.
 (i) If the pressure in two bulbs is same, calculate ratio of u_{rms} for them.
 (ii) At what temperature velocity of SO_2 becomes half of the speed of He molecules at $27^\circ C$?
 (iii) How will the speeds be effected if volume of B becomes four times?
- (iv) How will the speeds be effected if half of the molecules of SO_2 are removed from B ?
106. The kinetic molecular theory attributes an average translational kinetic energy of $\frac{3}{2} \frac{RT}{N}$ to each particle. What rms speed would a mist particle of mass 10^{-12} g have at room temperature ($27^\circ C$) according to kinetic theory of gases?
107. Two flasks A and B have equal volumes. Flask A contains H_2 at $27^\circ C$ while B contains equal mass of C_2H_6 at $627^\circ C$. In which flask and by how many times are molecules moving faster? Assume ideal gas nature for both.
108. Assuming O_2 molecule spherical in shape and occupying the radius 150 pm, calculate:
 (a) the volume of single molecule of gas.
 (b) the percentage of empty space in one mole of O_2 at NTP.
 (c) comment on the percentage of empty space.
109. During an experiment, an ideal gas is found to obey an additional law $PV^2 = \text{constant}$. The gas is initially at temperature T and volume V . Calculate the temperature when it expands to a volume $2V$.
110. For one mole of a gas if $P = \frac{P_0}{1 + \left(\frac{V}{V_0}\right)^2}$, where P_0 and V_0 are constant. Find the temperature of gas when $V = V_0$.
111. Calculate the volume correction and pressure correction for 4.4 g CO_2 kept in 1 litre flask. Given $a = 3.6 \text{ atm L}^2 \text{ mol}^{-2}$ and $b = 0.04 \text{ L mol}^{-1}$ for CO_2 .
112. The value of ' b ' for steam is $0.0305 \text{ litre mol}^{-1}$. The density of liquid water is 0.958 g/mL at $100^\circ C$. What % of volume of water molecules occupy in gaseous phase of water in liquid phase?
113. Calculate the percentage of free volume available in 1 mole gaseous water at 1.0 atm and $100^\circ C$. Density of liquid H_2O at $100^\circ C$ is 0.958 g/mL . Assume ideal gas behaviour.
114. Calculate the average volume available to a molecule in a sample of nitrogen gas at STP. What is the average distance between neighbouring molecules if nitrogen molecules are spherical in nature?
115. Calculate molecular diameter of He from its van der Waals' constant $b = 24 \text{ mL mol}^{-1}$.
116. Atomic and molecular sizes are of the order of a few angstrom ($1 \text{ \AA} = 10^{-10} \text{ m}$). Assuming that N_2 molecule is spherical in shape with radius $2 \times 10^{-10} \text{ m}$, calculate:
 (i) the volume of single N_2 molecule.
 (ii) the percentage of empty space in one mole of N_2 gas at STP.

117. Calculate the pressure exerted by 5 mole of CO_2 in one litre vessel at 47°C using van der Waals' equation. Also report the pressure of gas if it behaves ideally in nature. Given that $a = 3.592 \text{ atm litre}^2 \text{ mol}^{-2}$, $b = 0.0427 \text{ litre mol}^{-1}$.
118. If volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K . $a = 3.592 \text{ atm litre}^2 \text{ mol}^{-2}$. (IIT 2000)
119. The compression factor (compressibility factor) for 1 mole of a van der Waals' gas at 0°C and 100 atmosphere pressure is found to be 0.5. Assuming that the volume of gas molecule is negligible, calculate the van der Waals' constant. (IIT 2001)
120. Calculate the compressibility factor for CO_2 , if one mole of it occupies 0.4 litre at 300 K and 40 atm . Comment on the result.
121. The compressibility factor for a given real gas is 0.927 at 273 K and 100 atm . Calculate the mass of gas required to fill a gas cylinder of 100 litre capacity under given conditions. [Molar mass of gas = 30]
122. The density of the vapours of a substance at 1 atm pressure and 500 K is 0.36 kg m^{-3} . The vapour effuses through a small hole at a rate of 1.33 times faster than oxygen under the same condition.
- (a) Determine (i) molar mass, (ii) molar volume, (iii) compression factor (Z) of the vapours and (iv) which forces among the gas molecules are dominating, the attractive or the repulsive?
- (b) If the vapours behaves ideally at 1000 K , determine the average translational kinetic energy of molecules. (IIT 2002)
123. Using van der Waals' equation, calculate the constant, ' a ' when two mole of a gas confined in a four litre flask exerts a pressure of 11.0 atmospheres at a temperature of 300 K . The value of ' b ' is $0.05 \text{ litre mol}^{-1}$. (IIT 1998)
124. 5.6 litre of an unknown gas at NTP requires 12.5 calorie to raise its temperature by 10°C at constant volume. Calculate:
- (a) C_v of gas, (b) atomicity of gas.
125. Calculate the temperature of gas if it obeys van der Waals' equation from the following data. A flask of 25 litre contains 10 mole of a gas under 50 atm. Given $a = 5.46 \text{ atm litre}^2 \text{ mol}^{-2}$ and $b = 0.031 \text{ litre mol}^{-1}$.
126. Compressibility factor (Z) for N_2 at -50°C and 800 atm pressure is 1.95. Calculate mole of N_2 gas required to fill a gas cylinder of 100 mL capacity under the given conditions.
127. The critical constant for water are 374°C , 218 atm and $0.0566 \text{ litre mol}^{-1}$. Calculate a , b and R .
128. One way of writing the equation of state for real gases is:
- $$PV = RT \left[1 + \frac{B}{V} + \dots \right]$$
- where B is a constant. Derive an approximate expression for B in terms of van der Waals' constants a and b . (IIT May 1997)
129. A certain gas ' A ' polymerises to a small extent at a given P and T as $nA \rightleftharpoons [A]_n$. Show that the gas obeys the approximate equation $\frac{PV}{RT} \left[1 - \frac{(n-1)K_C}{V^{n-1}} \right]$ where $K_C = \frac{[A_n]}{[A]^n}$ and V is the volume of container. Initially 1 mole of ' A ' was taken in container.
130. The molar volume of He at 10.1325 MPa and 273 K is 0.011075 of its molar volume at 101.325 kPa at 273 K . Calculate the radius of helium atom. The gas is assumed to show real gas nature. Neglect the value of a for He.
131. A real gas is supposed to obey the gas equation $P(V-b) = nRT$ at STP. If one mole of a gas occupies, 25 dm^3 volume at STP, calculate:
- (a) diameter of each gas molecule.
- (b) compressibility factor for gas.
132. Calculate van der Waals' constants a and b if critical temperature and critical pressure are 30°C and 72 atm respectively.
133. The critical temperature of O_2 and N_2 are 155 K and 126 K respectively. Calculate the ratio of reduced temperature of O_2 and N_2 at 300 K .
134. Reduced temperature and reduced volume of benzene are 0.7277 and 0.40 respectively. Calculate reduced pressure of benzene.
135. van der Waals' constant a and b for hydrogen are $0.246 \text{ L}^2 \text{ atm mol}^{-2}$ and $0.0267 \text{ L mol}^{-1}$ respectively. Calculate inversion temperature and Boyle's temperature of H_2 gas.
136. A vacuum pump has a cylinder of volume v and is connected to a vessel of volume V to pump out air from the vessel. The initial pressure of gas in vessel is P . Show that after n strokes, the pressure in vessel is reduced to $P_n = P \left[\frac{V}{V+v} \right]^n$.
137. A graph is plotted between PV_m along y-axis and P along x-axis, where V_m is the molar volume of a real gas. Find the intercept along y-axis. (IIT 2004)
138. 1 g of He having rms speed 1000 m/s and 4 g of oxygen having rms speed 1000 m/s are introduced in a thermally isolated vessel. Find the rms speed of He and O_2 molecules when thermal equilibrium is attained.
139. The number of molecules in a gas sample that have the range of most probable speed (u_{mp}) at a temperature T is

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one half the number of same type of molecules that have the most probable speed at 300 K . What is T ?

140. A bottle contains 1.0 mol He(g) and a second bottle contains 1.0 mol Ar(g) at the same temperature. At this temperature, the root mean square speed of He is

Numerical Chemistry

1477 m s^{-1} and that of Ar is 467 m s^{-1} . What is the ratio of the number of He atoms in the first bottle to the number of Ar atoms in the second bottle having these speeds? Assume that both gases behave ideally.

SOLUTIONS (Numerical Problems)

1. Given, initially $V_2 = \frac{300}{1000}$ litre, $P_2 = \frac{730}{760}$ atm,

$$T_2 = 300 \text{ K}$$

At STP $V_1 = ?$, $P_1 = 1 \text{ atm}$, $T_1 = 273 \text{ K}$

$$\text{Now use, } \frac{P_2 V_2}{T_2} = \frac{P_1 V_1}{T_1}$$

$$V_1 = 0.2622 \text{ litre}$$

$\therefore$ Volume (V) at STP = 262.2 mL

2. Given, $P_1 = 1 \text{ atm}$, $V_1 = 2.5 \text{ litre}$, $T_1 = 273 \text{ K}$,

$$P_2 = 1.5 \text{ atm}, V_2 = 2.0 \text{ litre}, T_2 = ?$$

$$\text{Now use, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore T_2 = 327.6 \text{ K or } 54.6^\circ \text{ C}$$

3. Given, $w = 7 \text{ g}$, $T = 300 \text{ K}$, $P = \frac{750}{760} \text{ atm}$ and $M = 28 \text{ g mol}^{-1}$

$$\text{Now use, } PV = \frac{w}{M} RT \quad (R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1})$$

$$\therefore V = 6.239 \text{ litre}$$

4. $V \propto n$ also $V = kn$

$$\therefore 60 = k \times 3 \text{ or } k = 20.0$$

$$\Delta V = k \cdot \Delta n$$

$$\Delta V = 20 \times 0.1 = 2 \text{ litre}$$

5. $P = 16 \text{ atm}$, $V = 9 \text{ litre}$, $T = 300 \text{ K}$, $M = 16$

$$\text{Now use, } PV = \frac{w}{M} RT$$

$$\therefore w = 96 \text{ g}$$

6. For H_2 ,

$$w = 0.184 \text{ g}, T = 290 \text{ K at pressure } P \text{ and volume } V.$$

$$\therefore PV = \frac{0.184}{2} \times R \times 290 \quad \dots(1)$$

For the gas,

$$w = 3.7 \text{ g}, T = 298 \text{ K at pressure } P \text{ and volume } V$$

$$\therefore PV = \frac{3.7}{M} \times R \times 298 \quad \dots(2)$$

By Eqs. (1) and (2), $M = 41.326 \text{ g mol}^{-1}$

7. $w = 5 \text{ g}$, $M = 30$ for C_2H_6 , $V = 1 \text{ litre}$

Let the bulb bursts at T kelvin, i.e., when pressure becomes 10 atm.

$$\therefore PV = \frac{w}{M} RT \text{ so } 10 \times 1 = \frac{5}{30} \times 0.0821 \times T$$

$$\therefore T = 730.81 \text{ K} = 457.81^\circ \text{ C}$$

8. Volume occupied by solute at NTP

$$= \text{Volume of air displaced at NTP} = 112 \text{ mL}$$

$$\therefore \text{For volatile solute, } PV = \frac{w}{M} RT$$

$$\text{at NTP } P = 1 \text{ atm}, T = 273 \text{ K}$$

$$\therefore 1 \times \frac{112}{1000} = \frac{0.23}{M} \times 0.0821 \times 273$$

$$\therefore M = 46.02 \text{ g mol}^{-1} \text{ and V.D.} = 23.01$$

9. Given, $P_1 = P$, $V_1 = V$, $T_1 = T$

$$P_2 = P_2, V_2 = V - \frac{SV}{100}, T_2 = T$$

$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ or } P \times V = P_2 \times \left(V - \frac{SV}{100}\right)$$

$$\text{or } P_2 = \frac{100P}{95}$$

$$\therefore P_2 = 1.0526P$$

$$\therefore \text{Increase in } P = 0.0526$$

$$\therefore \% \text{ increase in } P = 0.0526 \times 100 = 5.26$$

10. $P = 7.6 \times 10^{-10} \text{ mm} = \frac{7.6 \times 10^{-10}}{760} \text{ atm}$

$$V = 1 \text{ litre}, T = 273 \text{ K}$$

$$\therefore PV = nRT$$

$$\frac{7.6 \times 10^{-10}}{760} \times 1 = n \times 0.0821 \times 273$$

$$\therefore n = 4.46 \times 10^{-14} \text{ mole of } \text{O}_2$$

$\therefore$ No. of molecule of

$$\text{O}_2 = 4.46 \times 10^{-14} \times 6.023 \times 10^{23} = 2.68 \times 10^{10}$$

11. Given, $P = \frac{2 \times 10^{-6}}{760} \text{ atm}$, $T = -180 + 273 = 93 \text{ K}$,

$$V = 1 \text{ mL} = \frac{1}{1000} \text{ litre}$$

$$\therefore PV = nRT$$

$$\frac{2 \times 10^{-6}}{760} \times 10^{-3} = n \times 0.0821 \times 93$$

$$\therefore n = 3.45 \times 10^{-13} \text{ mol}$$

12. Mass of gas in 1.5 litre

$$\text{or } 1.5 \times 10^{-3} \text{ m}^3 = 1.25 \times 1.5 \times 10^{-3} \text{ kg}$$

$$\text{New density} = \frac{\text{Mass}}{\text{New volume}} = \frac{1.25 \times 1.5 \times 10^{-3}}{3.92 \times 10^{-6}} \text{ kg/m}^3$$

$$= 478.3 \text{ kg/m}^3$$

13. Case I Given, $P = 1 \text{ atm}$, $w = 12 \text{ g}$, $T = (t + 273) \text{ K}$, $V = V \text{ litre}$

$$\text{Case II } T = (t + 283); P = 1 + \frac{10}{100} = 1.1 \text{ atm}, w = 12 \text{ g},$$

$$V = V \text{ litre}$$

Using gas equation :

$$\text{Case I } 1 \times V = \frac{12}{M} \times R (t + 273)$$

$$\text{Case II } 1.1 \times V = \frac{12}{M} \times R (t + 283)$$

$$\text{By Eqs. (1) and (2), } \frac{1.1}{1} = \frac{t + 283}{t + 273}$$

$$\therefore 1.1t + 300.3 = t + 283$$

$$\therefore 0.1t = -17.3$$

$$\therefore t = -173^\circ \text{ C} = 100 \text{ K}$$

$$\text{Also, from Case I } 1 \times V = \frac{12}{120} \times 0.082 \times 100 (\because M = 120)$$

$$V = 0.82 \text{ litre}$$

14. Given, $P_1 = 250 \text{ kPa}$, $T_1 = 300 \text{ K}$
 $P_2 = 1 \times 10^6 \text{ Pa}$, $T_2 = ?$

Since, volume of cylinder remains constant.

$$\text{Therefore, } \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{250 \times 10^3}{300} = \frac{1 \times 10^6}{T_2}$$

$$\therefore T_2 = 1200 \text{ K}$$

The cylinder will blow up at 1200 K before its melting (m.pt. 1800 K).

15. (a) At STP
 $V_1 = 95 \text{ mL} = \frac{95}{1000} \text{ litre}$
 $T_1 = 300 \text{ K}$
 $P_1 = 750 - 60 = 690 \text{ mm} = \frac{690}{760} \text{ atm}$
 $T_2 = 273 \text{ K}$
 $P_2 = \frac{760}{760} \text{ atm} = 1 \text{ atm}$
- $$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$
- $$\frac{690 \times 95}{760 \times 1000 \times 300} = \frac{1 \times V_2}{273}$$
- $$\therefore V_2 = 0.07848 \text{ litre} = 78.48 \text{ mL}$$

- (b) $V_2 = ?$, $T_2 = 313 \text{ K}$

$$P_2 = 745 + 25 = 770 \text{ mm} = \frac{770}{760} \text{ atm}$$

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

$$\frac{690 \times 95}{760 \times 300 \times 1000} = \frac{770 \times V_2}{760 \times 313}$$

$$\therefore V_2 = 0.0888 \text{ litre} = 88.8 \text{ mL}$$

16. Mass of butane in cylinder
 $= 29.0 - 14.8 = 14.2 \text{ kg} = 14.2 \times 10^3 \text{ g}$
 $P = 2.5 \text{ atm}$, $T = 300 \text{ K}$, Molar mass of butane = 58
 $\therefore PV = \frac{w}{M} RT$

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

$$\therefore V = 2.4 \times 10^3 \text{ litre} = 2.4 \text{ m}^3$$

This is volume of cylinder or volume of gas.

Now the mass of gas left after use

$$= 23.2 - 14.8 = 8.4 \text{ kg} = 8.4 \times 10^3 \text{ g}$$

The volume remains constant.

$$\text{Again using } PV = \frac{w}{M} RT$$

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

$$\therefore \text{Pressure (P) of the gas left in cylinder} = 1.50 \text{ atm}$$

Now, pressure of gas given out = 1

Mass of gas given out = 29.0 - 23.2

$$= 5.8 \text{ kg} = 5.8 \times 10^3 \text{ g}$$

Thus, volume of gas given out under these conditions is

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

$$\therefore V = 2.4 \times 10^3 \text{ litre} = 2.4 \text{ m}^3$$

17. Maximum capacity or volume of balloon

$$= \frac{8}{7} \times 480 = 548.57 \text{ mL}$$

Also, $V_1 = 480 \text{ mL}$, $T_1 = 278 \text{ K}$, $n = 1 \text{ mole}$

- (a) The balloon will burst at the temperature say T_2 when volume becomes 548.57 mL,

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

$$\frac{480}{278} = \frac{548.57}{T_2}$$

$$\therefore T_2 = 317.71 \text{ K} = 44.71^\circ \text{C}$$

Thus, balloon will not burst at 30°C .

- (b) The minimum temperature at which balloon bursts is 44.71°C

- (c) Pressure of gas at 5°C having 1 mole and $V = 480 \text{ mL}$

$$P \times \frac{480}{1000} = 1 \times 0.0821 \times 278$$

$$P = 47.5 \text{ atm}$$

- (d) Since, V increases with temperature rise from 5°C to 44.71°C at which the balloon bursts and therefore pressure remains constant. Thus pressure of gas in balloon when it bursts is 47.5 atm .

18. For B-H compound,

$$P = 0.658 \text{ atm}$$
, $V = \frac{407}{1000} \text{ litre}$, $T = 373 \text{ K}$, $w = 0.553 \text{ g}$

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

$$0.658 \times \frac{407}{1000} = \frac{0.553}{M} \times 0.0821 \times 373$$

$$M = 63.23 \text{ g mol}^{-1}$$

$\therefore 100 \text{ g}$ compound has 85.7 g B

$$\therefore 63.23 \text{ g compound has} = \frac{85.7 \times 63.23}{100} \text{ g B} = 54.19 \text{ g B}$$

$$= \frac{54.19}{10.8} \text{ g -atom of B} = 5 \text{ g -atom of B}$$

$\therefore$ Formula becomes B_5H_x

$$\therefore 5 \times 10.8 + x = 63.25$$

$$x = 9.25 = 9 \text{ (an integer)}$$

$\therefore$ Formula of compound is B_5H_9 .

19. $w = 1.98 \text{ g}$, $V = 1.47 \text{ litre}$, $T = 303 \text{ K}$

$$P = 744 - 32 = 712 \text{ mm} = \frac{712}{760} \text{ atm}$$

$$\therefore \text{For dry gas, } PV = \frac{w}{M} RT$$

$$\frac{712}{760} \times 1.47 = \frac{1.98}{M} \times 0.0821 \times 303$$

$$\therefore M = 35.76 \text{ g mol}^{-1}$$

20. $P = \frac{800}{760} \text{ atm}$, $T = 273 + 100 = 373 \text{ K}$

Let density be d for CO_2 .

$$\text{For } \text{CO}_2, \quad PV = \frac{w}{M} RT$$

$$\therefore P = \frac{d}{M} RT \quad \left(\because \frac{w}{V} = d \right)$$

- $$\frac{800}{760} = \frac{d}{44} \times 0.0821 \times 373$$

$$\therefore d = 1.5124 \text{ g litre}^{-1}$$
21. For mixture of CO and CO₂, $d = 1.50 \text{ g litre}^{-1}$

$$P = \frac{730}{760} \text{ atm}, \quad T = 303 \text{ K}$$

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

$$P = \frac{w}{VM} RT$$

$$\frac{730}{760} = \frac{1.50}{M} \times 0.0821 \times 303 \quad \left(\because \frac{w}{V} = d \right)$$

$$\therefore M = 38.85 \text{ g mol}^{-1}$$

i.e., Molar mass of mixture of CO and CO₂ = 38.85
 Let % of mole of CO be a in mixture, then
 Average mol. mass = $\frac{a \times 28 + (100 - a) \times 44}{100}$

$$38.85 = \frac{28a + 4400 - 44a}{100}$$

$$\therefore a = 32.19$$

$$\therefore \text{Mole \% of CO} = 32.19$$

$$\text{Mole \% of CO}_2 = 67.81$$

22. Volume of one balloon which is to be filled

$$= \frac{4}{3} \pi \left(\frac{21}{2} \right)^3 = 4851 \text{ mL} = 4.851 \text{ litre}$$

Let n balloons are filled, then volume of H₂ occupied by balloons

$$= 4.851 \times n$$

Also, cylinder will not be empty and it will occupy volume of

$$\text{H}_2 = 2.82 \text{ litre}$$

$$\therefore \text{Total volume occupied by H}_2 \text{ at NTP}$$

$$= 4.851 \times n + 2.82 \text{ litre}$$

Therefore, at STP available H₂

$$P_1 = 1 \text{ atm} \quad P_2 = 20 \text{ atm}$$

$$V_1 = 4.851 \times n + 2.82 \quad V_2 = 2.82 \text{ litre}$$

$$T_1 = 273 \text{ K} \quad T_2 = 300 \text{ K}$$

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

or

$$\frac{1 \times (4.851n + 2.82)}{273} = \frac{20 \times 2.82}{300}$$

$$\therefore n = 10$$

23. Mass of balloon = $100 \text{ kg} = 10 \times 10^4 \text{ g}$
 Volume of balloon = $\frac{4}{3} \pi r^3 = \frac{4}{3} \times \frac{22}{7} \times \left(\frac{20}{2} \times 100 \right)^3$

$$= 4190 \times 10^6 \text{ cm}^3 = 4190 \times 10^3 \text{ litre}$$

Mass of gas (He) in balloon = $\frac{PVM}{RT} \quad \left(\because PV = \frac{w}{M} RT \right)$

$$= \frac{1 \times 4190 \times 10^3 \times 4}{0.082 \times 300} = 68.13 \times 10^4 \text{ g}$$

$$\therefore \text{Total mass of gas and balloon}$$

$$= 68.13 \times 10^4 + 10 \times 10^4 = 78.13 \times 10^4 \text{ g}$$

$$\text{Mass of air displaced} = \frac{1.2 \times 4190 \times 10^6}{10^3} = 502.8 \times 10^4 \text{ g}$$

$$\therefore \text{Pay load} = \text{mass of air displaced} - (\text{mass of balloon} + \text{mass of gas})$$

$$\therefore \text{Pay load} = 502.8 \times 10^4 - 78.13 \times 10^4 = 424.67 \times 10^4 \text{ g}$$

24. For diatomic gas
 $V = 350 \text{ mL}, \quad P = 2 \text{ atm}, \quad T = 273 \text{ K}, \quad w = 1 \text{ g}$

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

$$2 \times \frac{350}{1000} = \frac{1}{M} \times 0.0821 \times 273$$

$$\therefore \text{Molar mass 'M' of gas} = 32.02$$

$$\therefore \text{Atomic mass of gas} = \frac{\text{molar mass}}{2} = \frac{32.02}{2} = 16.01$$

$$\therefore \text{Mass of 1 atm of gas} = \frac{16.01}{6.023 \times 10^{23}} = 2.66 \times 10^{-23} \text{ g}$$
25. Suppose at $T = 27^\circ \text{C} = 300 \text{ K}, \quad T_1 = 37^\circ \text{C} = 310 \text{ K},$
 $V = 1 \text{ litre}, \quad V_1 = ?$
 At constant pressure $\frac{V}{T} = \frac{V_1}{T_1}$

$$\frac{1}{300} = \frac{V_1}{310} \quad \therefore V_1 = \frac{310}{300} = 1.0333 \text{ litre}$$

Since, capacity of flask is 1 litre.

$$\therefore \text{Volume of air escaped out} = 1.0333 - 1 = 0.0333 \text{ litre} = 33.3 \text{ mL}$$

26. At $T_1 = 300 \text{ K}$, mole of air = n_1
 At $T_2 = 750 \text{ K}$, mole of air = n_2
 $\therefore$ At constant $P, V, \quad n_1 T_1 = n_2 T_2$

$$\therefore n_1 \times 300 = n_2 \times 750 \quad \text{or} \quad n_2 = \frac{300}{750} \times n_1$$

or

$$n_2 = 0.4 n_1$$

$$\therefore \text{Mole of air escaped out} = n_1 - n_2 = n_1 - 0.4 n_1 = 0.6 n_1$$

or fraction of air escaped out = 0.6

27. (a) Initial temperature = 300 K
 Let no. of mole at $300 \text{ K} = n$
 New temperature be $= T \text{ K}$

$$\therefore \text{Mole coming out at } T \text{ K} = \frac{1}{3} n$$

$$\therefore \text{Mole left at } T \text{ K} = n - \frac{1}{3} n = \frac{2}{3} n$$

Under constant P and $V, \quad n_1 T_1 = n_2 T_2$

$$\therefore n \times 300 = \frac{2}{3} n \times T$$

$$\therefore T = 450 \text{ K} = 177^\circ \text{C}$$

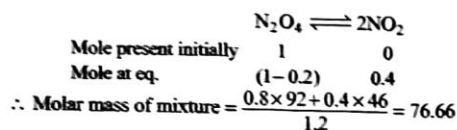
(b) Initial temperature = 300 K
 New temperature becomes $= T \text{ K}$
 Let no. of mole present at $T \text{ K} = n$
 Mole coming out at $T \text{ K} = \frac{1}{3} n$

$$\therefore \text{No. of mole at } 300 \text{ K should be} = n + \frac{1}{3} n = \frac{4n}{3}$$

$$\therefore \frac{4n}{3} \times 300 = n \times T$$

$$\therefore T = 400 \text{ K} = 127^\circ \text{C}$$

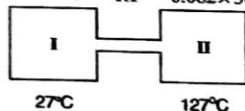
28.



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

or $\frac{w}{V} = \frac{PM}{RT} = \frac{76.66 \times 1}{0.082 \times 300} = 3.116 \text{ g litre}^{-1}$

29.



Two flasks initially at 27°C and 0.5 atm, have same volume and 0.7 mole; thus each flask has 0.35 mole. Let n mole of gas are diffused from II to I on heating the II flask at 127°C.

$\therefore$ Mole in I flask = $(0.35 + n)$
 and Mole in II flask = $(0.35 - n)$
 Thus, if new pressure of flask is P , then
 For I, $P_{\text{new}} \times V = (0.35 + n) \times R \times 300$
 For II, $P_{\text{new}} \times V = (0.35 - n) \times R \times 400$
 $\therefore n = 0.05$
 $\therefore$ Mole in flask I = $0.35 + 0.05 = 0.40$
 and Mole in flask II = $0.35 - 0.05 = 0.30$
 Also, $0.5 \times 2V = 0.7 \times 0.0821 \times 300$ (initial condition)
 $\therefore V = 17.241 \text{ litre}$
 Thus, $P_{\text{new}} \times 17.241 = 0.30 \times 0.0821 \times 400$
 $\therefore P = 0.5714 \text{ atm}$

30. (a) Mole of gas coming out on heating

$$n = \frac{PV}{RT} = \frac{1 \times 0.246}{0.0821 \times 300} = 0.009987$$

Thus, mole of gas left = $\frac{7.1}{71} - 0.009987 = 0.09$
 $= 0.1 - 0.009987 = 0.09$

Also, for 0.1 mole of gas $PV = 0.1RT$... (1)

for 0.09 mole of gas $PV = 0.09R(T + 30)$... (2)

By Eqs. (1) and (2), $T = 270 \text{ K}$

(b) Also, if gas is not allowed to escape, then for 0.1 mole of gas

$$P \times V = 0.10 \times R \times 270 \quad \dots (3)$$

$$(P + 0.11)V = 0.10 \times R \times 303 \quad \dots (4)$$

By Eqs. (3) and (4), $P = 0.99 \text{ atm}$

By Eq. (3), $0.99 \times V = 0.10 \times R \times 270$

$$\therefore V = 2.239 \text{ litre}$$

31. Given, $V = 10 \text{ litre}$, $P = 3 \text{ atm}$, $T = 290 \text{ K}$ (a) After driving $V = 10 \text{ litre}$, $P = ?$, $T = 320 \text{ K}$

$$\therefore \frac{P_1}{P_2} = \frac{T_1}{T_2} \quad (\text{at constant } V \text{ of tyre})$$

$$\frac{3}{P} = \frac{290}{320}$$

$$\therefore P = 3.31 \text{ atm}$$

(b) At 47°C

Now volume is to be taken out so that tyre is left at a pressure of 3 atm, i.e., decrease in pressure as a result of it,

$$= 3.31 - 3.0 = 0.31 \text{ atm}$$

At 0.31 atm volume of air is 10 litre and therefore, at 1 atm this air will occupy V litre

$$\therefore P_1 V_1 = P_2 V_2 \quad (\text{temperature is } 47^\circ \text{C})$$

$$\therefore 0.31 \times 10 = 1 \times V_2$$

$$\therefore V_2 = 3.1 \text{ litre}$$

32. Pressure at 100 meter depth

$$= \text{Atmospheric pressure} + \text{Pressure of water}$$

$$= 76 \times 13.6 \times 981 + 100 \times 100 \times 1 \times 981$$

$$= 1013961.6 + 9810000 = 10823961.6 \text{ dyne cm}^{-2}$$

Let volume of balloon at the surface level be $V_i \text{ cm}^3$ and the volume of balloon at the depth of 100 meter is V_f , then

$$P_1 V_1 = P_2 V_2$$

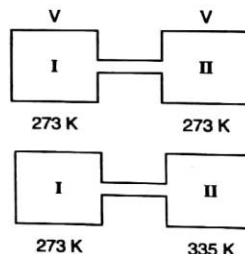
$$\therefore 76 \times 13.6 \times 981 \times V_f = 10823961.6 \times V_i$$

$$\therefore V_f = \frac{76 \times 13.6 \times 981}{10823961.6} \times V_i$$

$$V_f = 0.0937 V_i$$

$$\therefore V_f = 9.37\% \text{ of } V_i$$

33.



Initially when both bulbs are at 273 K, the mole in each bulb

$$= \frac{\text{Total mole}}{2} = \frac{P \cdot 2V}{2RT} = \frac{PV}{RT} = \frac{76 \times V}{R \times 273} \quad \dots (1)$$

On heating II bulb, some mole of gas are transferred to bulb I till the pressure in two bulbs becomes same

For bulb I, $n_1 = \frac{P_1 \times V}{R \times 273}$

For bulb II, $n_2 = \frac{P_2 \times V}{R \times 335}$

Since,

$$\therefore \frac{76 \times V}{R \times 273} \times 2 = \frac{P_1 \times V}{R \times 273} + \frac{P_2 \times V}{R \times 335} \quad \text{Also, } P_1 = P_2$$

$$\therefore P_1 = 83.75 \text{ cm of Hg}$$

34. Initial mole of air present = $\frac{PV}{RT}$

$$= \frac{75 \times 0.7}{76 \times 0.0821 \times 290}$$

$$(V = 0.2 + 0.5 = 0.7 \text{ litre})$$

$$= 0.029$$

Now, let n_2 mole are present in boiling water vessel and n_1 mole in melting ice vessel

$$\therefore n = 0.029 = n_1 + n_2$$

$$0.029 = \frac{P \times 0.2}{0.0821 \times 273} + \frac{P \times 0.5}{0.0821 \times 373}$$

(P remains same at equilibrium)

$$\therefore P = \frac{0.029}{8.92 \times 10^{-3} + 16.33 \times 10^{-3}}$$

$$= 1.15 \text{ atm} = \mathbf{87.4 \text{ cm of Hg}}$$

35. 98.4°F can be converted to $^\circ \text{C}$ as

$$\frac{F - 32}{9} = \frac{C}{5}$$

$$\frac{98.4 - 32}{9} = \frac{C}{5}$$

$$\therefore C = 36.88^\circ \text{C} \quad \text{or} \quad 309.88 \text{ K}$$

Thus using, $PV = \frac{w}{M} RT$

$$\frac{168}{760} \times 6 = \frac{w}{32} \times 0.0821 \times 309.88$$

$$\therefore w = 1.67 \text{ g}$$

36. Mole present initially in 1 L container

$$(n_1) = \frac{PV}{RT} = \frac{1000 \times 1}{760 \times 0.0821 \times 273} = 5.87 \times 10^{-2}$$

Mole present initially in 0.1 L container

$$(n_2) = \frac{PV}{RT} = \frac{1000 \times 0.1}{760 \times 0.0821 \times 273} = 5.87 \times 10^{-3}$$

$$\therefore n_1 + n_2 = 5.87 \times 10^{-2} + 5.87 \times 10^{-3} = 6.46 \times 10^{-2}$$

Also, on heating the vessel of 0.1 L to 373 K, let ' n ' mole remain in it, then since, pressure will remain the same, then $\frac{nRT}{V}$ is constant in both

$$\frac{n \times 373}{0.1} = \frac{(6.46 \times 10^{-2} - n) \times 273}{1}$$

$$\therefore n = 4.40 \times 10^{-3}$$

i.e., mole left in 0.1 litre container after heating = 4.40×10^{-3}

$\therefore$ Mole moved from 0.1 L to 1 L vessel

$$= 5.87 \times 10^{-2} - 4.40 \times 10^{-3}$$

$$= 1.47 \times 10^{-2}$$

$\therefore$ Volume of air moved at 0°C and 760 mm

$$V = \frac{nRT}{P} = \frac{1.47 \times 10^{-2} \times 0.0821 \times 273}{1}$$

$$= \mathbf{32.9 \text{ mL}}$$

37. I flask : Volume = 2 litre, $P_{N_2} = 70 \text{ cm}$, $T = 293 \text{ K}$

II flask : Volume = 3 litre, $P_{O_2} = 100 \text{ cm}$, $T = 293 \text{ K}$

Before mixing

$$\text{Mole of } N_2 = \frac{PV}{RT} = \frac{70 \times 2}{76 \times 0.0821 \times 293} = 7.658 \times 10^{-2}$$

$$\text{Mole of } O_2 = \frac{PV}{RT} = \frac{100 \times 3}{76 \times 0.0821 \times 293} = 16.41 \times 10^{-2}$$

After mixing total volume becomes 5 litre.

$$\therefore P_{N_2} = \frac{nRT}{V} = \frac{7.658 \times 10^{-2} \times 0.0821 \times 293}{5} = 0.368 \text{ atm}$$

$$P_{O_2} = \frac{nRT}{V} = \frac{16.41 \times 10^{-2} \times 0.0821 \times 293}{5} = 0.79 \text{ atm}$$

$$\therefore P_M = P_{N_2} + P_{O_2} = 0.368 + 0.79 = \mathbf{1.158 \text{ atm}}$$

$$\text{Mole \% of } N_2 = \frac{7.658 \times 10^{-2}}{(7.658 + 16.41) \times 10^{-2}} \times 100 = \mathbf{31.8\%}$$

$$\therefore \text{Mole \% of } O_2 = \mathbf{68.2\%}$$

38. Given, $V = 10 \text{ litre}$, $T = 27 + 273 = 300 \text{ K}$

$$\text{Mole of He} = \frac{0.4}{4} = 0.10$$

$$\text{Mole of } O_2 = \frac{1.6}{32} = 0.05$$

$$\text{Mole of } N_2 = \frac{1.4}{28} = 0.05$$

$$\therefore \text{Total mole} = 0.10 + 0.05 + 0.05 = 0.20$$

$$P_M = \frac{nRT}{V} = \frac{0.20 \times 0.0821 \times 300}{10} = 0.492 \text{ atm}$$

$$P_{He} = P_M \times \text{mole fraction of He} = 0.492 \times \frac{0.10}{0.20}$$

$$= \mathbf{0.246 \text{ atm}}$$

$$P_{O_2} = P_M \times \text{mole fraction of } O_2 = 0.492 \times \frac{0.05}{0.20}$$

$$= \mathbf{0.123 \text{ atm}}$$

$$P_{N_2} = P_M \times \text{mole fraction of } N_2 = 0.492 \times \frac{0.05}{0.20}$$

$$= \mathbf{0.123 \text{ atm}}$$

39. Given, mass of CH_4 = mass of O_2 = $w \text{ g}$, $V = 1 \text{ litre}$, $T = 300 \text{ K}$

$$(a) \text{ Mole fraction of } CH_4 = \frac{w/16}{w/16 + w/32} = \frac{2}{3}$$

$$\text{Mole fraction of } O_2 = \frac{w/32}{w/16 + w/32} = \frac{1}{3}$$

$$\therefore P_{O_2} = P_M \times \text{mole fraction of } O_2$$

(Dalton's law of partial pressure)

$$\therefore \frac{P_{O_2}}{P_M} = \text{mole fraction of } O_2 = \frac{1}{3}$$

$$(b) P_{CH_4} \times 1 = (32/16) \times 0.0821 \times 300 = 49.26 \text{ atm}$$

$$P_{O_2} \times 1 = (32/32) \times 0.0821 \times 300 = 24.63 \text{ atm}$$

$$\therefore P_M = P_{CH_4} + P_{O_2} = 49.26 + 24.63 = \mathbf{73.89 \text{ atm}}$$

40. Given, mass of gas A = 0.50 g, Molar mass of gas A = 60
mass of gas B = 0.2 g, Molar mass of gas B = 45

$$P_M = 750 \text{ mm}$$

From Dalton's law of partial pressure

$$P_A = P_M \times \text{mole fraction of A}$$

$$= 750 \times \frac{0.5/60}{\left(\frac{0.5}{60}\right) + \left(\frac{0.2}{45}\right)} = \mathbf{489.23 \text{ mm}}$$

$$\text{Now, } P_M = P_A + P_B$$

$$\therefore P_B = P_M - P_A = 750 - 489.23 = \mathbf{260.77 \text{ mm}}$$

41. $w = 20 \text{ g}$ dry CO_2 which will evaporate to develop P .

$$M = 44 \text{ g mol}^{-1}, V = 0.75 \text{ litre}, P = ?, T = 298 \text{ K}$$

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

$$P \times 0.75 = \frac{20}{44} \times 0.0821 \times 298$$

$$\therefore P = 14.828 \text{ atm}$$

NOTE : Pressure inside the bottle = P + atm. pressure

$$= 14.828 + 1 = 15.828 \text{ atm}$$

42. Let mass of $O_2 = w_1$
mass of $N_2 = w_2$

$$\therefore \text{Given, } \frac{w_1}{w_2} = \frac{1}{4}$$

Also, Mole of $O_2 = \frac{w_1}{32}$

$$\text{Mole of } N_2 = \frac{w_2}{28}$$

$$\therefore \frac{\text{Mole of } O_2}{\text{Mole of } N_2} = \frac{w_1}{32} \times \frac{28}{w_2} = \frac{28}{32} \times \frac{1}{4} = \frac{7}{32} \quad \left(\because \frac{w_1}{w_2} = \frac{1}{4} \right)$$

43. The water vapours occupy the volume of N_2 gas, i.e., 50 litre.

$\therefore$ For H_2O vapour $V = 50$ litre, $w = 1.20$ g, $T = 300$ K, $m = 18$

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

$$P \times 50 = \frac{1.2}{18} \times 0.0821 \times 300$$

$$P = 0.03284 \text{ atm}$$

$$= 24.95 \text{ mm}$$

44. According to Dalton's law of partial pressure,

Given, $P_M = 740$ mm, $P_{H_2O} = 18$ mm

$$P_M \text{ or } P_{\text{wet } O_2} = P_{O_2} + P_{H_2O}$$

$$740 = P_{O_2} + 18$$

$$\therefore P_{O_2} = 722 \text{ mm}$$

45. Partial pressure of O_2 , $P'_{O_2} = P_m \times \text{mole fraction}$

Since, $P_m = 1$ atm (given, NTP condition)

$$\therefore P'_{O_2} = 1 \times \text{mole fraction} \quad \dots(1)$$

$$\text{For mixture } PV = \frac{w}{M} RT$$

$$\therefore M = \frac{w}{VP} RT$$

$$M = \frac{1.3 \times 0.0821 \times 273}{1} \quad \left(\because \frac{w}{V} = 1.3 \text{ g L}^{-1} \right)$$

$$\therefore \text{Molar mass of mixture} = 29.137 \text{ g mol}^{-1}$$

If n_1 and n_2 are mole of O_2 and N_2 respectively,

$$\text{Now, } \frac{32 \times n_1 + 28 \times n_2}{(n_1 + n_2)} = 29.137$$

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

$$\therefore \frac{n_1}{n_1 + n_2} = \frac{29.137 - 28}{4} = 0.28$$

$$\therefore \text{Mole fraction of } O_2 = 0.28$$

$$\therefore \text{By Eq. (1), } P'_{O_2} = 0.28 \text{ atm}$$

46. Mass of liquid = $148 - 50 = 98$ g

$$\text{Volume of liquid} = \frac{98}{0.98} = 100 \text{ mL} = \text{volume of vessel}$$

Thus, a vessel of 100 mL contains ideal gas at 760 mm of Hg at 300 K.

$$\text{Mass of gas} = 50.5 - 50 = 0.5 \text{ g}$$

Using,

$$PV = nRT$$

$$\frac{760}{760} \times \frac{100}{1000} = \frac{0.5}{m} \times 0.0821 \times 300$$

$$\therefore \text{Molar mass of gas (m)} = 123$$

47. At T K, $P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}}$

$$\therefore P_{\text{dry gas}} = 830 - 30 = 800 \text{ mm}$$

$$\text{Now at new temperature } T_1 = T - \frac{T}{100} = 0.99 T$$

$$\text{Since, } V_1 = V_2; \frac{P}{T} = \text{constt.}$$

$$\therefore P_{\text{dry gas}} = \frac{800 \times 0.99 T}{T} = 792 \text{ mm}$$

$$\therefore P_{\text{gas}} = P_{\text{dry gas}} + P_{\text{moisture}} = 792 + 25 = 817 \text{ mm of Hg}$$

48. Given, mass of gas $A = 2$ g

Pressure of $A = 1$ atm, $T = 298$ K

Now another gas is introduced

mass of gas $B = 3$ g

Pressure of mixture = 1.5 atm

From Dalton's law of partial pressure

$$P_M = P'_A + P'_B$$

$$1.5 = 1.0 + P'_B$$

$$P'_B = 0.5 \text{ atm}$$

(a) For gas A , $P'_A \times V = \frac{2}{M_A} \times RT$

For gas B , $P'_B \times V = \frac{3}{M_B} \times RT$

$$\therefore \frac{P'_A}{P'_B} = \frac{2}{3} \times \frac{M_B}{M_A}$$

$$\therefore \frac{M_A}{M_B} = \frac{2}{3} \times \frac{P'_B}{P'_A} = \frac{2}{3} \times \frac{0.5}{1.0} = \frac{1}{3}$$

(b) If A is O_2 , molar mass of $O_2 = 32$

$$\therefore P'_A \times V = \frac{2}{32} \times 0.0821 \times 298$$

$$1 \times V = \frac{2}{32} \times 0.0821 \times 298$$

$$V = 1.529 \text{ litre}$$

49. Average molar mass = $\frac{35n_1 + 37n_2}{n_1 + n_2} = 35.45$

where, n_1 and n_2 are mole of Cl^{35} and Cl^{37} isotopes.

$$\therefore \frac{n_1}{n_2} = 3.44$$

$$\therefore P \times V_1 = n_1 RT$$

$$P \times V_2 = n_2 RT$$

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

Now volume $\propto$ mole, when other things being equal and thus partition should be made at the point where mole ratio is 3.44 : 1. Pressure at this condition is same as the original pressure ($\because V, T, n$ are constant).

50. $P_{\text{air}} = 760 \text{ mm at } 285 \text{ K}$,

$$\therefore P_{\text{air}} = 760 - 10.5 = 749.5 \text{ mm Hg}$$

$$P_{\text{air}} = 760 \text{ mm at } 308 \text{ K}, \therefore P_{\text{air}} = 760 - 42 = 718 \text{ mm Hg}$$

Length of the air = 10 cm at 285 K

$$\therefore \text{Volume of the air} = 10 \times a \quad (\text{where, } a \text{ is area of tube})$$

Let h be the length of air column at 308 K

$$\therefore \frac{718 \times h \times a}{n \times R \times 308}$$

$$749.5 \times 10 \times a = n \times R \times 285$$

$$\therefore h = \frac{308}{285} \times \frac{749.5 \times 10}{718} = 11.28 \text{ cm}$$

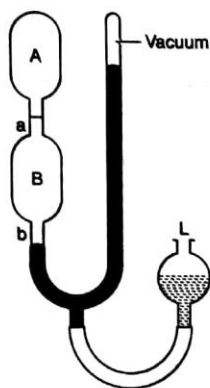
51. Given, $P = 10^{-16} \text{ mm}$, $V = 1 \text{ litre}$, $T = 273 - 120 = 153$

$$\therefore PV = nRT$$

$$\therefore n = \frac{PV}{RT} = \frac{10^{-16} \times 1}{760 \times 0.0821 \times 153} = 1.05 \times 10^{-20}$$

$$\therefore \text{Number of Hg-atom} = 6.023 \times 10^{23} \times 1.05 \times 10^{-20} = 6324 \text{ atom per litre}$$

52.



Pressure of He = 20.14 mm

Temperature of He = 273 + 30.2 = 303.2 K

Volume of He = 110 + 100.5 = 210.5 cm³

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

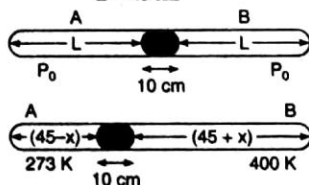
$$\therefore w = \frac{PVM}{RT} = \frac{20.14 \times 210.5 \times 4}{760 \times 0.0821 \times 303.2 \times 1000}$$

$$w_{\text{He}} = 8.96 \times 10^{-4} \text{ g}$$

53. According to problem

Initially $2L + 10 = 100$

$$\therefore L = 45 \text{ cm}$$



Let initial pressure be P_0 atm on each side. When one end is cooled and other is heated, expansion of gas occurs at hotter end till the pressure on two sides becomes same. Let Hg column is displaced by x cm to cooler end,

$$\text{i.e., } P_1 = P_2 = P$$

$$\text{Now for end A: } \frac{P_0 \times 45 \times a}{300} = \frac{P_1 (45-x) \times a}{273} \quad \dots(1)$$

because mole of gas remains same at 273 and 300 K; a is area of cross-section of tube.

$$\text{For end B: } \frac{P_0 \times 45 \times a}{300} = \frac{P_2 (45+x) \times a}{400} \quad \dots(2)$$

Evaluating P_1 and P_2 from Eqs. (1) and (2) and since

$$\frac{P_1}{P_2} = \frac{P_1}{P_2} = \frac{273 \times 45 \times P_0}{300 \times (45-x)} = \frac{400 \times 45 \times P_0}{300 \times (45+x)}$$

$$\therefore x = 8.49 \text{ cm}$$

Thus, length of air column at 0°C

$$= 45 - 8.49 = 36.51 \text{ cm}$$

Length of air column at 127°C = 45 + 8.49 = 53.49 cm

$$\text{Also, pressure } (P) = P_1 = \frac{273 \times 45 \times 76}{300 \times 36.51} = 85.25 \text{ cm of Hg}$$

54. Let initially the length of air column on each side be L , then

$$2L + 10 = 100$$

$$\therefore L = 45 \text{ cm}$$

If the tube is held vertically, let the Hg column be displaced downwards by y to attain same pressure above and below the column of Hg. Then,

$$P_B + 10 = P_A \quad \dots(1)$$

Pressure are taken in terms of length of Hg.

For end A: Since mole remains same on two sides

$$\frac{P_0 \times L \times a}{RT} = \frac{P_A \times (L-y) \times a}{RT} \quad \dots(2)$$

$$\therefore P_A = \frac{LP_0}{(L-y)} \quad \dots(3)$$

For end B:

$$\frac{P_0 \times L \times a}{RT} = \frac{P_B \times (L+y) \times a}{RT} \quad \dots(4)$$

$$\therefore P_B = \frac{LP_0}{(L+y)} \quad \dots(5)$$

By Eqs. (1), (3) and (5)

$$\left[\frac{LP_0}{L+y} \right] + 10 = \frac{LP_0}{(L-y)}$$

Putting $L = 45 \text{ cm}$ and $P_0 = 76 \text{ cm}$

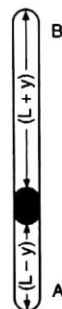
$$y^2 + 684y - (45)^2 = 0$$

$$\therefore y = 3 \text{ cm}$$

55. Case I, at 300 K:

Let pressure in upper half be P_1 and lower half be P_2 . Also P_0 is pressure of piston

$$\text{At equilibrium } P_2 = P_0 + P_1 \quad \dots(1)$$



Let volume of cylinder be V litre

$$\therefore \text{Volume of upper half} = \frac{4V}{5}$$

$$\text{and Volume of lower half} = \frac{V}{5}$$

Also in the two parts of cylinder, each part contains 1 mole at 300 K and thus,

$$P_1 \times \frac{4V}{5} = P_2 \times \frac{V}{5}$$

$$\therefore \frac{P_2}{P_1} = 4 \quad \dots(2)$$

$$\text{By Eqs. (1) and (2), } P_1 = \frac{P_0}{3} \quad \dots(3)$$

Case II, at T K :

Now the temperature becomes T at which volume of upper half is $\frac{3V}{4}$ and lower half is $\frac{V}{4}$.

$$\text{Again } P_1' \times \frac{3V}{4} = P_2' \times \frac{V}{4}$$

$$\therefore \frac{P_2'}{P_1'} = 3 \quad \dots(4)$$

$$\text{By Eqs. (1) and (4), } P_1' = \frac{P_0}{2} \quad \dots(5)$$

Now using $PV = nRT$ for upper parts of cylinder at 300 K and T K

$$P_1 \times \frac{4V}{5} = 1 \times R \times 300$$

Case I upper part

$$P_1' \times \frac{3V}{4} = 1 \times R \times T$$

Case II upper part

$$\therefore \frac{P_1}{P_1'} \times \frac{16}{15} = \frac{300}{T} \quad \dots(6)$$

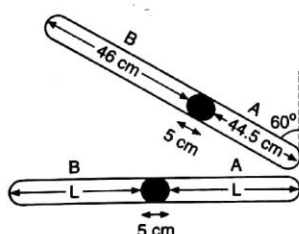
$$\text{Using Eqs. (3) and (5) in Eq. (6), } \frac{2}{3} \times \frac{16}{15} = \frac{300}{T}$$

$$\therefore T = \frac{300 \times 3 \times 15}{2 \times 16} = 421.875 \text{ K}$$

56. Let initially the length of air column in tube be L cm, then

$$2L + 5 = 46 + 5 + 44.5$$

$$\therefore L = 45.25 \text{ cm}$$



When the tube is held vertically at 60° , the Hg will be displaced to lower end, so that

$$P_B + 5 \cos 60^\circ = P_A$$

$$\text{or } P_A - P_B = 5 \times \frac{1}{2} = 2.5 \text{ cm of Hg} \quad \dots(1)$$

$$\text{For end A: } \frac{P_0 \times a \times 45.25}{RT} = \frac{P_A \times 44.5 \times a}{RT}$$

$$\therefore P_A = \frac{45.25}{44.5} \times P_0 \quad \dots(2)$$

$$\text{For end B: } \frac{P_0 \times a \times 45.25}{RT} = \frac{P_B \times a \times 46}{RT}$$

$$\therefore P_B = \frac{45.25}{46} \times P_0 \quad \dots(3)$$

Also by Eqs. (1), (2) and (3) $P_0 = 75.4 \text{ cm of Hg}$

57. The mole of air contained in bubble at the bottom of tank as well as on the surface remains same.

$$\text{Thus, } n = \frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2}$$

At bottom of the tank At the surface

$$\text{or } \frac{3 \times \frac{4}{3} \pi \times (0.5)^3}{R \times 278} = \frac{1 \times \frac{4}{3} \pi r^3}{R \times 298}$$

$$\therefore r = 0.74 \text{ cm}$$

58. Given, $P_{N_2} + P_{H_2O} = 760 \text{ mm}$

H_2O is dried by drying agent and left pressure stands for N_2 .

$$\text{Thus, } P_{N_2} = 745 \text{ mm}$$

$$\therefore P_{H_2O} = 760 - 745 = 15 \text{ mm}$$

- (a) Since, $P_{N_2} = P_M \times \text{mole fraction of } N_2$

$$\therefore \text{Mole fraction of } N_2 = \frac{745}{760} = 0.9803$$

$$\text{or \% mole fraction of } N_2 = 98.03\%$$

$$\therefore \text{\% mole fraction of } H_2O = 1.97\%$$

- (b) The mass of H_2O in mixture = increase in mass of drying agent

$$= 0.15 \text{ g}$$

$$\therefore \text{Mole of } H_2O (n) = \frac{0.15}{18}$$

Now use $PV = nRT$ for water vapours, in a flask of volume V .

$$\frac{15}{760} \times V = \frac{0.15}{18} \times 0.0821 \times 293$$

$$(\because T = 273 + 20 = 293 \text{ K})$$

$$\therefore V = 10.16 \text{ litre}$$

59. $N_2 \rightleftharpoons 2N$

$$\text{Initial mole } \frac{1.4}{28} \quad 0$$

$$\text{Mole after dissociation } \frac{1.4}{28} \times \frac{70}{100} \quad \frac{1.4}{28} \times \frac{2 \times 30}{100}$$

$$\therefore \text{Total mole} = \frac{1.4}{28} \times \frac{70}{100} + \frac{1.4 \times 60}{100 \times 28} = \frac{1.4}{28} \times \left[\frac{130}{100} \right]$$

$$\therefore P \times 5 = \frac{1.4 \times 130}{28 \times 100} \times 0.0821 \times 1800$$

$$\therefore P = 1.92 \text{ atm}$$

60. Initially at lower end :

$$P = 76 \text{ cm of Hg} + 76 \text{ cm of air} = 152 \text{ cm}, T = 300 \text{ K}, V = \frac{V_1}{2}$$

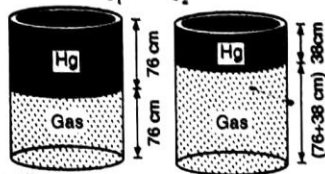
where V_1 is volume of cylinder

Finally at lower end :

$$P = 76 \text{ cm of air} + 38 \text{ cm of Hg} = 114 \text{ cm}, \quad T = ?$$

$$V = \frac{3V_1}{4}$$

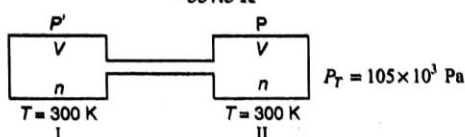
$$\therefore \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$



$$\frac{152 \times V_1}{2 \times 300} = \frac{114 \times 3V_1}{4 \times T}$$

$$\therefore T = \frac{114 \times 3 \times 2 \times 300}{152 \times 4} = 337.5 \text{ K}$$

61.



Let each vessel contains n mole initially since, both are at same conditions.

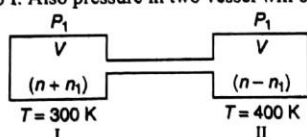
$$P' \times V = nR \times 300 \quad \dots(1)$$

$$P \times V = nR \times 300 \quad \dots(2)$$

$$P' + P = P_T = 105 \times 10^3 \text{ Pa}$$

$$\therefore 2n \times R \times 300 = 105 \times 10^3 \times V \quad \dots(3)$$

On putting one vessel at 400 K, mole from this vessel will move to the vessel at 300 K. Let n_1 mole move from II vessel to I. Also pressure in two vessel will be same.



$$P_1 \times V = (n + n_1) \times R \times 300 \quad n > n_1 \quad \dots(4)$$

$$P_1 \times V = (n - n_1) \times R \times 400 \quad \dots(5)$$

$$\therefore \frac{n + n_1}{n - n_1} = \frac{400}{300}$$

$$300n + 300n_1 = 400n - 400n_1$$

$$n_1 = \frac{1}{7}n$$

$$\text{Vessel I has, } n + \frac{n}{7} \text{ mole} = \frac{8n}{7}$$

$$\text{Vessel II has, } n - \frac{n}{7} \text{ mole} = \frac{6n}{7}$$

$$\therefore \text{Ratio of mole in vessel I and II} = \frac{8}{6} = \frac{4}{3}$$

$$\text{By Eqs. (3) and (4)} \quad \frac{2n \times R \times 300}{8 \frac{n}{7} \times R \times 300} = \frac{105 \times 10^3 \times V}{P_1 \times V}$$

$$\therefore P_1 = \frac{105 \times 10^3 \times 8}{2 \times 7} = 60000 \text{ Pa}$$

$$\therefore \text{Total pressure} = 2P_1 = 2 \times 60000 = 120000 \text{ Pa} = 120 \text{ kPa}$$

62.



The aqueous tension remains same in both the flask. Also flasks are at same temperature.

$$\text{Thus, } \frac{P_1 V_1}{(\text{Initially})} = \frac{P_2 V_2}{(\text{Finally})}$$

$$\text{Initial pressure of gas } P_1 = 200 - 93 = 107 \text{ mm}$$

$$\text{Final pressure of gas} = P$$

$$\therefore 107 \times 1 = P \times 2 \quad \therefore P = \frac{107}{2} = 53.5 \text{ mm}$$

Since, aqueous tension or P'_{H_2O} , is also present in flasks, equivalent to 93 mm.

$$\therefore \text{Pressure of gaseous mixture} = 93 + 53.5 = 146.5 \text{ mm}$$

$$63. \quad P_{\text{wet air}} = 760 \text{ mm at } 298 \text{ K}$$

$$P_{\text{dry air}} = 760 - 24 = 736 \text{ mm at } 298 \text{ K}$$

$$\text{Now } \frac{P_1}{P_2} = \frac{T_1}{T_2} \quad (\text{The temperature is raised to } 100^\circ \text{C})$$

$$\frac{P_1}{736} = \frac{373}{298}$$

$$\therefore P_1 = 921.23 \text{ mm Hg}$$

$$P_{\text{wet air at } 100^\circ \text{C}} = P_1 + P_{H_2O} \text{ at } 373 \text{ K} = 921.23 + 760 = 1681.23 \text{ mm Hg}$$

64. Using

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

[For saturation vapour pressure of water = $3.6 \times 10^3 \text{ Pa}$, $V = 1 \text{ litre} = 1 \times 10^{-3} \text{ m}^3$]

$$3.6 \times 10^3 \times 10^{-3} = \frac{w_{H_2O}}{18} \times 8.314 \times 300$$

$$\therefore w_{H_2O} = 0.026 \text{ kg} = 26 \text{ g}$$

Since, relative humidity is 50%.

Thus, mass of water vapour is $26 \times 0.5 = 13 \text{ g}$

$$65. \quad \text{For dry air: } P_{(N_2 + O_2)} = 760 \text{ mm}$$

$$\therefore P_{N_2} = \frac{760 \times 79}{100} = 600.40 \text{ mm}$$

$$P_{O_2} = \frac{760 \times 21}{100} = 159.60 \text{ mm}$$

Let volume be 1 litre, then

$$\text{mole of } N_2 = \frac{PV}{RT} = \frac{600.4 \times 1}{760 \times 0.0821 \times 298} = 3.23 \times 10^{-2}$$

$$\text{mole of } O_2 = \frac{159.6 \times 1}{760 \times 0.0821 \times 298} = 8.58 \times 10^{-3}$$

$$\therefore \text{Density of dry air} = \text{mass of dry air in one litre} \\ = 3.23 \times 10^{-2} \times 28 + 8.58 \times 10^{-3} \times 32 \\ = 90.44 \times 10^{-2} + 27.46 \times 10^{-2} \\ = 1.179 \text{ g/litre}$$

For moist air:

$$\therefore \text{Partial pressure of water} = \frac{60}{100} \times 23.76 = 14.3 \text{ mm}$$

$$\therefore \text{Partial pressure of } (N_2 + O_2) = 760 - 14.3 = 745.7 \text{ mm}$$

$$\therefore P_{N_2} = 745.7 \times \frac{79}{100} = 589.1 \text{ mm}$$

$$\therefore P_{O_2} = 745.7 \times \frac{21}{100} = 156.6 \text{ mm}$$

Let the volume be 1 litre, then

Mole of water vapours

$$(n_1) = \frac{PV}{RT} = \frac{14.3 \times 1}{760 \times 0.082 \times 298} = 7.7 \times 10^{-4}$$

$$\text{Mole of } N_2 (n_2) = \frac{589.1 \times 1}{760 \times 0.082 \times 298} = 3.17 \times 10^{-2}$$

$$\text{Mole of } O_2 (n_3) = \frac{156.6 \times 1}{760 \times 0.082 \times 298} = 8.43 \times 10^{-3}$$

$\therefore$ Total mass in one litre

$$= 7.7 \times 10^{-4} \times 18 + 3.17 \times 10^{-2} \times 28 + 8.43 \times 10^{-3} \times 32 = 1.171 \text{ g}$$

$$\therefore \text{Density of moist air at } 25^\circ \text{C} = 1.171 \text{ g litre}^{-1}$$

66. Given volume of container = 0.731 mL

$$\text{Temperature} = 23 + 273 = 296 \text{ K}$$

$$P_{H_2O_v} + P_{CO_2} + P_{N_2} = 1.74 \text{ mm} \quad \dots(1)$$

When H_2O_v is frozen out, the pressure exists for CO_2 and N_2 and therefore,

$$P_{CO_2} + P_{N_2} = 1.32 \text{ mm} \quad \dots(2)$$

When CO_2 is frozen out, the pressure exist for N_2 only and therefore,

$$P_{N_2} = 0.53 \text{ mm} \quad \dots(3)$$

By Eqs. (1), (2) and (3),

$$P_{CO_2} = 0.79 \text{ mm}, \quad P_{H_2O_v} = 0.42 \text{ mm}$$

Now for N_2 , $PV = nRT$

$$\therefore n = \frac{PV}{RT} = \frac{0.53 \times 0.731}{760 \times 1000 \times 0.0821 \times 296} = 2.1 \times 10^{-8}$$

$$\text{Similarly for } CO_2 \quad n = 3.1 \times 10^{-8}$$

$$\text{and } H_2O \quad n = 1.7 \times 10^{-8}$$

67. Given, pressure of $N_2 = 0.965 \text{ atm}$

Volume of $N_2 = 10 \text{ litre}$, Temperature of $N_2 = 298 \text{ K}$

$\therefore$ For N_2 when bag is fully expanded,

$$\text{Volume of } N_2 \text{ (alone)} = 30 \text{ litre at } 298 \text{ K}$$

$$\therefore P_1 V_1 = P_2 V_2$$

$$0.965 \times 10 = P_2 \times 30$$

$$\therefore P_{N_2} \text{ (alone) in } 30 \text{ litre bag at } 298 \text{ K} = 0.322 \text{ atm}$$

Now

$$P_M = P_{O_2} + P_{N_2}$$

$$0.990 = P_{O_2} + 0.322$$

$$\therefore P_{O_2} = 0.668 \text{ atm}$$

$$68. \quad P_{N_2} + P_{NO} + P_{NO_2} = 3.0 \text{ cm} \quad \dots(1)$$

$$P_{N_2} + P_{NO} + P'_{H_2O} = 2.42 \text{ cm} \quad \dots(2)$$

(H_2O absorbs NO_2 and P'_{H_2O} exist in gases)

$$P_{N_2} + P'_{H_2O} = 1.24 \text{ cm} \quad \dots(3)$$

($FeSO_4$ absorbs NO and P'_{H_2O} exists in gases)

$$\text{Given } P'_{H_2O} = 0.2 \text{ cm and } P'_{H_2O} = 0.18 \text{ cm}$$

$$\therefore \text{By Eq. (3)} \quad P_{N_2} = 1.24 - 0.18 = 1.06 \text{ cm} \quad \dots(4)$$

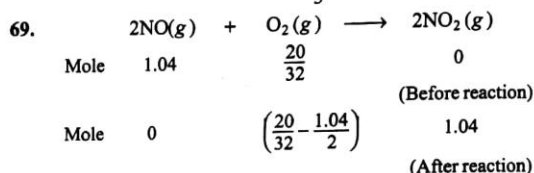
$$\text{By Eq. (2) and (3)} \quad P_{NO} = 2.42 - 1.06 - 0.2 = 1.16 \text{ cm}$$

$$P_{NO_2} = 3.0 - 1.06 - 1.16 = 0.78 \text{ cm}$$

$$\therefore \text{Mole \% of } N_2 = \frac{1.06}{3} \times 100 = 35.33$$

$$\text{Mole \% of } NO = \frac{1.06}{3} \times 100 = 38.67$$

$$\text{Mole \% of } NO_2 = \frac{0.78}{3} \times 100 = 26.00$$



$$\therefore \text{Total mole before reaction} = 1.04 + \frac{20}{32} = 1.665$$

$$\text{Total mole after reaction} = \frac{20}{32} - \frac{1.04}{2} + 1.04 = 1.145$$

$\therefore$ Change in no. of mole during reaction

$$= 1.665 - 1.145 = 0.520$$

$\therefore$ Change in pressure

$$= \frac{\Delta nRT}{V} = \frac{0.52 \times 0.0821 \times 300}{20} = 0.64 \text{ atm}$$

70. Given reaction is $2H_2 + O_2 \longrightarrow 2H_2O(l)$

$$\text{Volume before reaction} \quad a \quad b \quad 0$$

$$\text{Volume after reaction} \quad (a - 2b) \quad 0$$

Since at constant P and T , gases react in their volume ratio

$$\text{Given } a + b = 40, \quad a - 2b = 10$$

$$\therefore a = 30 \text{ mL}, \quad b = 10 \text{ mL}$$

Therefore, mole % of H_2

$$= \text{Volume \% of } H_2 = \frac{30}{40} \times 100 = 75\%$$

71. $2NH_3 \longrightarrow N_2 + 3H_2$

(a) Since no. of mole after reaction (n_2) = 2 $\times$ no. of mole before reaction (n_1) at same T and V , $P \propto n$

$$\therefore \frac{P_1}{P_2} = \frac{n_1}{n_2} = \frac{1}{2}$$

$\therefore$ Pressure after reaction = 2 atm

(b) Given for NH_3 , $p = 1 \text{ atm}$, $V = 1 \text{ litre}$, $T = 298 \text{ K}$

$$\therefore \text{Mole of } NH_3 = \frac{PV}{RT} = \frac{1 \times 1}{0.0821 \times 298} = 4.087 \times 10^{-2}$$

$$\therefore \text{Mole of } N_2 \text{ formed} = \text{Mole of } NH_3 \times \frac{1}{2}$$

$$= \frac{4.087 \times 10^{-2}}{2} = 2.0435 \times 10^{-2}$$

$$\therefore \text{Mole of } H_2 \text{ formed} = \text{Mole of } NH_3 \times \frac{3}{2}$$

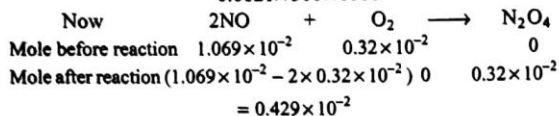
$$= \frac{4.087 \times 10^{-2} \times 3}{2} = 6.1305 \times 10^{-2}$$

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

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

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

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



$$\therefore \text{Mole of NO left} = 4.29 \times 10^{-3}$$

$$P_{\text{NO}} \times V = nRT$$

Given $T = 220 \text{ K}$, $V = \frac{250 + 100}{1000} = \frac{350}{1000} \text{ litre}$

$$P_{\text{NO}} \times \frac{350}{1000} = 4.29 \times 10^{-3} \times 0.0821 \times 220$$

$$\therefore P_{\text{NO}} \text{ left} = 0.221 \text{ atm}$$

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

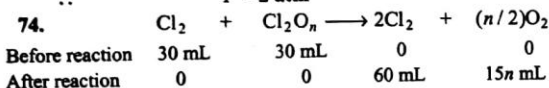
$$\therefore \text{Mole of } A = \frac{96}{2} \times \frac{1}{48} = 1 \quad \left(n = \frac{w}{m}\right)$$

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

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

Thus, $PV = nRT$
 $P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546$

$$\therefore P = 2 \text{ atm}$$

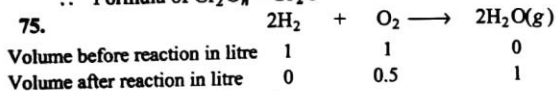


The volume of O_2 = Volume left after passing mixture through KOH (KOH absorbs Cl_2)
 $= 5$

$$\therefore 15n = 15$$

$$\therefore n = 1$$

$$\therefore \text{Formula of } \text{Cl}_2\text{O}_n = \text{Cl}_2\text{O}$$



(a) Mole of H_2O formed
 $= \frac{PV}{RT} = \frac{1 \times 1}{0.0821 \times 273} = 4.46 \times 10^{-2}$

$$\therefore \text{Mass of } \text{H}_2\text{O} \text{ formed} = 4.46 \times 10^{-2} \times 18 = 8.03 \times 10^{-1} \text{ g}$$

(b) Gas left is $\text{O}_2 = 0.5 \text{ litre at STP} = 2.23 \times 10^{-2} \text{ mole}$

$$\therefore \text{Mass of } \text{O}_2 \text{ left} = \frac{32 \times 0.5}{22.4} \text{ g} = 0.7143 \text{ g}$$

(c) At 100°C H_2O also exists as vapours

$$\therefore \text{Total mole present at } 100^\circ \text{C} = \text{mole of } \text{H}_2\text{O} \text{ formed} + \text{mole of } \text{O}_2 \text{ left} = 4.46 \times 10^{-2} + 2.23 \times 10^{-2} = 6.69 \times 10^{-2}$$

Volume of vessel = 2 litre

$$\therefore P = \frac{nRT}{V} = \frac{6.69 \times 10^{-2} \times 0.0821 \times 373}{2} = 1.02 \text{ atm}$$

(d) Volume of O_2 used for formation of $\text{H}_2\text{O} = 0.5 \text{ litre}$

$$\therefore \text{Mole of } \text{O}_2 \text{ used for formation of } \text{H}_2\text{O} = \frac{0.5}{22.4} = 2.23 \times 10^{-2}$$

$$76. \text{Mol. mass of mixture} = \frac{30 \times 4 + 20 \times 32 + 50 \times 28}{100} = 21.60$$

Also, rate of diffusion in terms of change of P/sec for Ne = 0.3 torr/sec

Let rate of diffusion in terms of change of P/sec for mixture be = r_2 torr/sec

$$\therefore \frac{0.3}{r_2} = \sqrt{\frac{21.60}{20}}$$

$$\text{or } r_2 = 0.289 \text{ torr/sec}$$

$$77. \frac{n_1}{n_2} = \frac{V_1}{V_2} \times \frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

$$\text{or } \frac{20}{60} \times \frac{30}{V} = \sqrt{\frac{32}{64}}$$

$$\therefore V = 14.14 \text{ dm}^3$$

78. For gaseous mixture 80% O_2 , 20% gas

$$\therefore \text{Average molar mass of mixture } (M_m) = \frac{32 \times 80 + 20 \times m}{100} \quad \dots(1)$$

Now for diffusion of gaseous mixture and pure O_2

$$\frac{r_{\text{O}_2}}{r_m} = \sqrt{\frac{M_m}{M_{\text{O}_2}}}$$

$$\text{or } \frac{V_{\text{O}_2}}{t_{\text{O}_2}} \times \frac{t_m}{V_m} = \sqrt{\frac{M_m}{M_{\text{O}_2}}} \quad (\because \text{same volume diffuses})$$

$$\therefore \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_m}{32}}$$

$$M_m = 34.92 \quad \dots(2)$$

By Eqs. (1) and (2), molar mass of gas $m = 46.6$

$$79. \frac{n_1}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

$$\text{or } \frac{n_1}{t_1} \times \frac{t_2}{n_2} = \sqrt{\frac{M_2}{M_1}} \times \frac{P_1}{P_2}$$

$$\text{or } \frac{1}{38} \times \frac{57}{1} = \sqrt{\frac{M_g}{28}} \times \frac{0.8}{1.6}$$

$$\therefore M_g = \left[\frac{57}{38} \times \frac{1.6}{0.8} \right]^2 \times 28$$

$$M_g = 252;$$

Thus, compound is XeF_6 because it can have only one xenon atom (since for two xenon atom, $2 \times \text{Atomic mass of Xe} = 2 \times 131 = 262$, i.e., greater than 252).

80. $P = 4.18 \text{ bar}$, $V = 3 \text{ L}$, $T = 300 \text{ K}$

$$R = 0.083 \text{ bar-litre K}^{-1} \text{ mol}^{-1}$$

$$\therefore n_T = \frac{PV}{RT} = \frac{4.18 \times 3}{0.083 \times 300}$$

$$n_T = 0.50$$

Total mole of gases diffused = 0.50

Mole of unknown gas n_g diffused

$$= n_T - n_{N_2} = 0.50 - 0.40 = 0.10$$

$$\text{Now, } \frac{n_g}{n_{N_2}} \times \frac{t_{N_2}}{t_g} = \sqrt{\frac{M_{N_2}}{M_g}} \quad (t_{N_2} = t_g = 10 \text{ min})$$

$$\text{or } \frac{0.1}{0.4} = \sqrt{\frac{28}{M_g}}$$

$$\therefore M_g = 448 \text{ g mol}^{-1}$$

81. Given

$$\frac{n_1}{n_2} = \frac{1}{4}, \quad \frac{w_1}{w_2} = \frac{2}{3}$$

We have

$$\frac{n_1}{n_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\therefore \frac{1}{4} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{M_2}{M_1} = \frac{1}{16}$$

Also, mole ratio

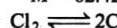
$$= \frac{n_1}{n_2} = \frac{w_1/M_1}{w_2/M_2} = \frac{w_1}{w_2} \times \frac{M_2}{M_1} = \frac{2}{3} \times \frac{1}{16} = \frac{1}{24}$$

82.

$$\frac{\gamma_{\text{mix}}}{\gamma_{\text{Kr}}} = \sqrt{\frac{M_{\text{Kr}}}{M_{\text{mix}}}} \quad \text{or} \quad 1.16 = \sqrt{\frac{84}{M}}$$

$$\therefore M = 62.425$$

For



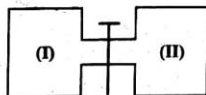
$$\begin{matrix} 1 & 0 \\ (1-\alpha) & 2\alpha \end{matrix}$$

$$\frac{\text{Normal molar mass}}{\text{Exp. molar mass}} = 1 + \alpha$$

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

$$\therefore \alpha = 0.137 \quad \text{or} \quad 13.7\%$$

83.



At STP

Before diffusion

$$\left. \begin{array}{l} \text{D}_2 = 1.12 \text{ lit. at STP} = 0.2 \text{ g} = 0.05 \text{ mole} \\ \text{H}_2 = 2.24 \text{ lit. at STP} = 0.2 \text{ g} = 0.1 \text{ mole} \end{array} \right\} \text{ in I bulb}$$

When these mole are placed in the bulb, the partial pressure of gas will be different because V and T are constant. Also $P \propto n$

$$\text{Thus, } \frac{P_{\text{D}_2}}{P_{\text{H}_2}} = \frac{0.05}{0.10} = \frac{1}{2}$$

After diffusion D_2 left in I bulb = 0.1 g

or D_2 diffuses from I into II (bulb) = $0.2 - 0.1 = 0.1$

Now for diffusion of D_2 and H_2

$$\frac{n_{\text{D}_2}}{n_{\text{H}_2}} = \sqrt{\frac{M_{\text{H}_2}}{M_{\text{D}_2}}} \times \frac{P_{\text{D}_2}}{P_{\text{H}_2}}$$

$$\therefore \frac{w_{\text{D}_2}}{t_{\text{D}_2}} \times \frac{t_{\text{H}_2}}{w_{\text{H}_2}} = \sqrt{\frac{M_{\text{D}_2}}{M_{\text{H}_2}}} \times \frac{P_{\text{D}_2}}{P_{\text{H}_2}}$$

$$\therefore \frac{0.1}{t} \times \frac{t}{w_{\text{H}_2}} = \sqrt{\frac{4}{2}} \times \frac{1}{2} \quad \therefore w_{\text{H}_2} = 0.14 \text{ g}$$

$\therefore$ Mass of gases in II bulb

$$= \text{mass of D}_2 + \text{mass of H}_2 = 0.10 \text{ g} + 0.14 \text{ g} = 0.24 \text{ g}$$

$$\therefore \% \text{ D}_2 \text{ by mass} = \frac{0.10}{0.24} \times 100 = 41.66\%$$

$$\% \text{ H}_2 \text{ in bulb II} = 58.33\%$$

84. Molar mass of $^{235}\text{UF}_6 = 235 + 19 \times 6 = 349$

Molar mass of $^{238}\text{UF}_6 = 238 + 19 \times 6 = 352$

From Graham's law at same P and T

$$\frac{n_1}{n_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{r_{\text{UF}_6}^{235}}{r_{\text{UF}_6}^{238}} = \sqrt{\frac{352}{349}} = 1.0043$$

$$\text{Also, } x = \frac{2 \log \left(\frac{n'_A/n'_B}{n_A/n_B} \right)}{\log \left(\frac{M_B}{M_A} \right)}$$

Here, $n_B = \text{U}^{235}$ in $\text{U}^{235}\text{F}_6 = 0.72$ and $M_B = M_{\text{U}^{235}\text{F}_6}$

$n_B = \text{U}^{238}$ in $\text{U}^{238}\text{F}_6 = 99.28$ and $M_A = M_{\text{U}^{238}\text{F}_6}$

$$n'_A = \text{U}^{235} \text{ in } \text{U}^{235}\text{F}_6 = 10$$

$$n'_B = \text{U}^{238} \text{ in } \text{U}^{238}\text{F}_6 = 90$$

$$\therefore x = \frac{2 \log \left[\frac{(10/90)}{(0.72/99.28)} \right]}{\log \left(\frac{352}{349} \right)}$$

$$x = 638 \text{ steps}$$

85. H_2 present has $^1\text{H}^1\text{H}$ and $^1\text{H}^2\text{H}$ in the ratio 99.8% and 0.2, i.e., $n_{2\text{H}} : n_{3\text{H}}$. This has to be diffused to have the outcoming sample enriched to 99.8% $^1\text{H}^1\text{H}$.

$$n_{2\text{H}} = 90 \quad n_{3\text{H}} = 10 \quad \therefore \frac{n_A}{n_B} = \frac{90}{10}$$

$$n_{2\text{H}}^1 = 99.8 \quad n_{3\text{H}}^1 = 0.2 \quad \therefore \frac{n'_A}{n'_B} = \frac{99.8}{0.2}$$

$$\therefore \text{Separation factor} = \frac{99.8 \times 10}{0.2 \times 90} = 55.44$$

$$\therefore f = \frac{r_{2\text{H}}}{r_{3\text{H}}} = \sqrt{\frac{M_{3\text{H}}}{M_{2\text{H}}}} = \sqrt{\frac{3}{2}}$$

Now, $(f'')^x = \left[\frac{n_A^1/n_B^1}{n_A^2/n_B^2} \right]$

$\therefore \left[\sqrt{\frac{3}{2}} \right]^x = 55.44$

$\therefore \frac{x}{2} \log \frac{3}{2} = 55.44$

$x = 19.8 \approx 20 \text{ steps}$

86. At constant V and T for a gas $P \propto w$

Thus, for N_2 : $P_1 = 2 \text{ atm}$, $P_2 = \frac{1}{2} \text{ atm}$, at $t = 1 \text{ hr}$, $w_1 = 14 \text{ kg}$,

$w_2 = ?$

$\therefore \frac{P_1}{P_2} = \frac{w_1}{w_2}; \quad \frac{2}{1/2} = \frac{14}{w_2}$

$\therefore w_2 = \frac{14}{4} \text{ kg } N_2$

$\therefore \text{mass of } N_2 \text{ diffused} = 14 - \frac{14}{4} = \frac{42}{4} = \frac{21}{2} \text{ kg}$

Similarly, for H_2 : $P_1 = 2 \text{ atm}$, $P_2 = \frac{1}{2} \text{ atm}$, at

$t = t \text{ hr}$, $w_1 = 1 \text{ kg}$, $w_2 = ?$

$\therefore \frac{P_1}{P_2} = \frac{w_1}{w_2}$

$\frac{2}{1/2} = \frac{1}{w_2} \quad \therefore w_2 = \frac{1}{4} \text{ kg}$

$\therefore \text{mass of } H_2 \text{ diffused} = 1 - \frac{1}{4} = \frac{3}{4} \text{ kg}$

Now $\frac{r_{N_2}}{r_{H_2}} = \sqrt{\left(\frac{M_{H_2}}{M_{N_2}} \right)}$

for diffusion of N_2 and H_2

or $\frac{w_{H_2}}{w_{N_2}} \times \frac{t_{N_2}}{t_{H_2}} = \sqrt{\left(\frac{M_{H_2}}{M_{N_2}} \right)}$

$\frac{3/4}{21/2} \times \frac{60}{t} = \sqrt{\left(\frac{2}{28} \right)} \quad (t_{N_2} = 1 \text{ hour} = 60 \text{ minute})$

$\therefore t = 16 \text{ minute}$

87. Mole of H_2 diffused = 0.7 in 20 minute

Mole of gas diffused = n_1 in 20 minute

For gaseous mixture after diffusion

$PV = nRT$
 $n = \frac{6 \times 3}{0.0821 \times 300} = 0.731$

$\therefore$ Mixture contains, mole of H_2 + mole of gas diffused = n

$\therefore 0.7 + n_1 = 0.731$

$\therefore n_1 = 0.031$

Now $\frac{r_{H_2}}{r_g} = \sqrt{\left(\frac{M_g}{M_{H_2}} \right)}$

$\frac{r_{H_2}}{t} \times \frac{t}{n_g} = \sqrt{\left(\frac{M_g}{2} \right)}$

$\frac{0.7}{20} \times \frac{20}{0.031} = \sqrt{\left(\frac{M_g}{2} \right)}$

$\therefore \frac{M_g}{2} = \frac{0.7 \times 0.7}{0.031 \times 0.031}$

$\therefore M_g = 1019.77$

88. Before diffusion:

Mole of $CO = 0.5$

Mole of $CO_2 = 0.5$

Total mole diffused out = A

Mole of CO diffused = a

Mole of CO_2 diffused = b

$a + b = A \quad \dots(1)$

Let

$\therefore$

Then,

Now,

M_1 = Mean molar mass of diffused portion

$M_1 = \frac{a \times 28 + 44 \times b}{(a+b)} = \frac{28a + 44b}{A} \quad \dots(2)$

Also, M_2 = Mean molar mass of left portion

$\frac{(0.5-a) \times 28 + (0.5-b) \times 44}{(0.5-a) + (0.5-b)} = \frac{14 - 28a + 22 - 44b}{1 - (a+b)}$
 $= \frac{36 - 28a - 44b}{1 - A}$

using Eq. (1)

$M_2 = \frac{36}{1-A} - \frac{28a + 44b}{1-A}$

$M_2 = \frac{36}{1-A} - \frac{M_1 A}{1-A}$

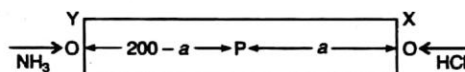
using Eq. (2)

$M_2(1-A) = 36 - M_1 A$

or

$M_1 A + M_2(1-A) = 36$

89.



Let distance of P from X end is $a \text{ cm}$.

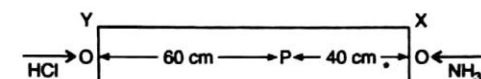
For diffusion of NH_3 and HCl at same P

$\frac{d_{NH_3}}{d_{HCl}} \times \frac{t_{HCl}}{t_{NH_3}} = \sqrt{\left(\frac{M_{HCl}}{M_{NH_3}} \right)}$

$\frac{200-a}{t} \times \frac{t}{a} = \sqrt{\left(\frac{36.5}{17} \right)} \quad (\text{time is same})$

$a = 81.1 \text{ cm}$

90.



For diffusion of NH_3 and HCl

Let pressure of $HCl = P \text{ atm}$

Let pressure of $NH_3 = 1 \text{ atm}$

$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\left(\frac{M_{HCl}}{M_{NH_3}} \right)} \times \frac{P_{NH_3}}{P_{HCl}}$

$$\frac{d_{\text{NH}_3}}{d_{\text{HCl}}} \times \frac{t_{\text{HCl}}}{t_{\text{NH}_3}} = \sqrt{\left(\frac{M_{\text{HCl}}}{M_{\text{NH}_3}}\right)} \times \frac{P_{\text{NH}_3}}{P_{\text{HCl}}}$$

$$\frac{40}{t} \times \frac{t}{60} = \sqrt{\left(\frac{36.5}{17}\right)} \times \frac{1}{P} \quad (\text{time is same})$$

$$\therefore P = 2.198 \text{ atm}$$

91. 2000 mm pressure of $\text{O}_2 \xrightarrow{t=47 \text{ min}} 1500 \text{ mm}$
 4000 mm pressure of mixture $\xrightarrow{t=74 \text{ min}} 1:1 (\text{O}_2 + \text{gas})$

For pure O_2 ,

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

When n_1 and n_2 are original no. of mole of O_2 and mole of O_2 after 47 minute.

$$\therefore \frac{n_1}{n_2} = \frac{2000}{1500}$$

$$\therefore n_2 = (3/4)n_1$$

$$\text{or mole of } \text{O}_2 \text{ diffused in 47 min} = n_1 - \frac{3n_1}{4} = \frac{n_1}{4}$$

$$\text{or mole of } \text{O}_2 \text{ diffused in 74 min} = \frac{n_1 \times 74}{47 \times 4}$$

$$= 0.3936 \quad (\text{if } n_1 = 1)$$

Since, diffusion of O_2 in mixture also occurs at partial pressure of 2000 mm. (The ratio of gas and O_2 being 1:1)
 Now gas and O_2 both diffusing in form of mixture through same orifice at the partial pressure of 2000 mm each.

$$\therefore \frac{n_{\text{O}_2}}{74} \times \frac{74}{n_g} = \sqrt{\left(\frac{79}{32}\right)}$$

$$\therefore n_g = n_{\text{O}_2} \times \sqrt{\left(\frac{32}{79}\right)} = \frac{74}{188} \times \sqrt{\left(\frac{32}{79}\right)} = 0.249$$

$$\therefore \text{Mole of } \text{O}_2 \text{ left after 74 minute} = 1 - 0.3936 = 0.6064$$

$$\text{Mole of gas left after 74 minute} = 1 - 0.249 = 0.7510$$

$$\therefore \text{O}_2 : \text{gas} :: 0.6064 : 0.7510$$

$$:: 1 : 1.236$$

92. Molar ratio of He and CH_4 is 4:1

$\therefore$ Partial pressure ratio of He and CH_4 is 16:4
 ($\because$ total pressure = 20 bar)

$$\frac{n_{\text{He}}}{n_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} \times \frac{P_{\text{He}}}{P_{\text{CH}_4}}$$

($\because$ time of diffusion for both is same)

$$= \sqrt{\frac{16}{4}} \times \frac{16}{4} = 8:1$$

The composition of mixture initially gone out for He and CH_4 is 8:1

$$93. u_{\text{rms}} = \sqrt{\frac{n_1 u_1^2 + n_2 u_2^2 + n_3 u_3^2 + \dots}{n_1 + n_2 + n_3 + \dots}}$$

$$= \sqrt{\frac{5 \times (15 \times 10^2)^2 + 10 \times (5 \times 10^2)^2 + 15 \times (10 \times 10^2)^2}{5 + 10 + 15}}$$

$$= 9.79 \times 10^2 \text{ m sec}^{-1}$$

$$\text{Also, } u_{\text{AV}} = \frac{n_1 u_1 + n_2 u_2 + n_3 u_3 + \dots}{n_1 + n_2 + n_3 + \dots}$$

$$= \frac{(5 \times 15 \times 10^2) + (10 \times 5 \times 10^2) + (15 \times 10 \times 10^2)}{5 + 10 + 15}$$

$$= 9.17 \times 10^2 \text{ m sec}^{-1}$$

94. If T is given always use

$$u_{\text{rms}} = \sqrt{\left(\frac{3RT}{M}\right)}$$

- (a) at STP $T = 273 \text{ K}$

$$\therefore u_{\text{rms}} \text{ for } \text{O}_2 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 273}{32}\right)}$$

$$= 4.61 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{Now } u_{\text{MP}} = u_{\text{rms}} \times 0.816 \quad \text{---(1)}$$

$$\text{and } u_{\text{AV}} = u_{\text{rms}} \times 0.9213 \quad \text{---(2)}$$

$$\therefore u_{\text{MP}} = 3.76 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{and } u_{\text{AV}} = 4.25 \times 10^4 \text{ cm sec}^{-1}$$

$$(b) u_{\text{rms}} \text{ of } \text{C}_2\text{H}_6 = \sqrt{\left(\frac{3RT}{M}\right)}$$

$$M = 30, \quad T = 27 + 273 = 300 \text{ K}$$

$$\therefore u_{\text{rms}} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 300}{30}\right)}$$

$$u_{\text{rms}} = 4.99 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{By Eq. (1), } u_{\text{MP}} = 4.07 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{By Eq. (2), } u_{\text{AV}} = 4.60 \times 10^4 \text{ cm sec}^{-1}$$

$$(c) u_{\text{rms}} \text{ of } \text{O}_2 = \sqrt{\left(\frac{3RT}{M}\right)}$$

$$\text{at } T = 17 + 273 = 290 \text{ K}$$

$$u_{\text{rms}} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 290}{32}\right)}$$

$$= 4.75 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{By Eq. (1), } u_{\text{MP}} = 3.88 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{By Eq. (2), } u_{\text{AV}} = 4.38 \times 10^4 \text{ cm sec}^{-1}$$

- (d) Density of $\text{O}_2 = 0.0081 \text{ g mL}^{-1} = 0.0081 \text{ g cm}^{-3}$

$$\text{and } P = 1 \text{ atm} = 1 \times 76 \times 13.6 \times 981 \text{ dyne cm}^{-2}$$

$$\text{Now, } u_{\text{rms}} = \sqrt{\left(\frac{3P}{d}\right)} = \sqrt{\left(\frac{3 \times 1 \times 76 \times 13.6 \times 981}{0.0081}\right)}$$

$$= 1.94 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{By Eq. (1), } u_{\text{MP}} = 1.58 \times 10^4 \text{ cm sec}^{-1}$$

$$\text{By Eq. (2), } u_{\text{AV}} = 1.78 \times 10^4 \text{ cm sec}^{-1}$$

- (e) Given for O_2 , $w = 6.431 \text{ g}$, $V = 5 \text{ litre}$

$$P = 750 \text{ mm} = 75 \text{ cm} = \frac{75}{76} \text{ atm}$$

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

$$\frac{75}{76} \times 5 = \frac{6.431}{32} \times 0.0821 \times T$$

$$\therefore T = 299.05 \text{ K}$$

- Now

$$u_{rms} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 299.05}{32}\right)}$$

$$u_{rms} = 4.83 \times 10^4 \text{ cm sec}^{-1}$$
 By Eq. (1), $u_{MP} = 3.94 \times 10^4 \text{ cm sec}^{-1}$
 By Eq. (2), $u_{AV} = 4.45 \times 10^4 \text{ cm sec}^{-1}$
 (f) For O_3 : $T = 20 + 273 = 293 \text{ K}$

$$\therefore u_{rms} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 293}{48}\right)}$$

$$u_{rms} = 3.9 \times 10^4 \text{ cm sec}^{-1}$$
 By Eq. (1), $u_{MP} = 3.18 \times 10^4 \text{ cm sec}^{-1}$
 By Eq. (2), $u_{AV} = 3.59 \times 10^4 \text{ cm sec}^{-1}$
 95. $u_{AV} = \sqrt{\left(\frac{8RT}{\pi M}\right)}$, $u_{MP} = \sqrt{\left(\frac{2RT}{M}\right)}$
 Average speed at $T_1 \text{ K} = \text{MP speed at } T_2 \text{ K for } CO_2$

$$\sqrt{\left(\frac{8RT_1}{\pi M}\right)} = \sqrt{\left(\frac{2RT_2}{M}\right)}$$

$$\therefore \frac{T_1}{T_2} = \frac{\pi}{4} \quad \dots(1)$$
 Also, for CO_2 $u_{MP} = \sqrt{\left(\frac{2RT}{M}\right)} = 9 \times 10^4$

$$\therefore \sqrt{\left(\frac{2 \times 8.314 \times 10^7 \times T_2}{44}\right)} = 9 \times 10^4$$

$$\therefore T_2 = 2143.37 \text{ K}$$

$$\therefore \text{By Eq. (1), } T_1 = 1684.0 \text{ K}$$

 96. $u_{AV} = \sqrt{\left(\frac{8RT}{\pi M}\right)}$
 Given $u_{AV} = 0.3 \text{ m sec}^{-1}$ at 300 K

$$\therefore u_1 = 0.3 = \sqrt{\left(\frac{8R \times 300}{\pi M}\right)} \quad \dots(1)$$
 at $T = 273 + 927 = 1200 \text{ K}$

$$\therefore u_2 = \sqrt{\left(\frac{8R \times 1200}{\pi M}\right)} \quad \dots(2)$$

$$\therefore \frac{u_2}{0.3} = \sqrt{\left(\frac{1200}{300}\right)}$$

$$\therefore u_2 = 0.6 \text{ m sec}^{-1}$$

 97. $u_{rms} = \sqrt{\left(\frac{3RT}{M}\right)}$, $u_{AV} = \sqrt{\left(\frac{8RT}{\pi M}\right)}$, $u_{MP} = \sqrt{\left(\frac{2RT}{M}\right)}$

$$\therefore u_{rms} : u_{AV} : u_{MP} = 1 : \sqrt{\left(\frac{8}{3\pi}\right)} : \sqrt{\left(\frac{2}{3}\right)}$$

$$= 1 : 0.9213 : 0.816$$
 Also $u_{MP} : u_{AV} : u_{rms} = 1 : \sqrt{(4/\pi)} : \sqrt{(3/2)}$

$$= 1 : 1.128 : 1.224$$

 98. $u_{AV} = \sqrt{\left(\frac{8RT}{\pi M}\right)} \quad \dots(1)$

- $$u_{rms} = \sqrt{\left(\frac{3RT}{M}\right)} \quad \dots(2)$$
- By Eqs. (1) and (2),
- $u_{rms} = u_{AV} \times \sqrt{\frac{3\pi}{8}}$
-
- $$= 400 \times \sqrt{\frac{3 \times 3.14}{8}} = 434 \text{ m/sec}$$
-
99. Given,
- $m_A = 2m_B$
-
- $\therefore$
- Molar mass of
- $A = 2 \times$
- Molar mass of
- B
- $\dots(1)$
-
- Given
- u_{rms}
- of
- $A = 2 \times u_{rms}$
- of
- B
- $\dots(2)$
-
- Also no. of molecules of
- $A =$
- No. of molecules of
- B
- $\dots(3)$
-
- For gas
- A
- $P_A V_A = \frac{1}{3} M_A u_{rms A}^2$
-
- For gas
- B
- $P_B V_B = \frac{1}{3} M_B u_{rms B}^2$
-
- $$\therefore \frac{P_A V_A}{P_B V_B} = \frac{M_A}{M_B} \times \frac{u_A^2}{u_B^2} \quad \dots(4)$$
- Given
- $V_A = V_B$
- $\dots(5)$
-
- $\therefore$
- By Eqs. (1), (2), (4) and (5),
- $\frac{P_A}{P_B} = 2 \times (2)^2 = 8$
-
- $$\therefore P_A = 8P_B$$
-
100. For gas
- $PV = \frac{w}{M} RT$
-
- $$3 \times 12.5 = \frac{15}{M} \times 0.0821 \times T$$
- $$\therefore \frac{T}{M} = 30.45$$
- Now
- $u_{AV} = \sqrt{\left(\frac{8RT}{\pi M}\right)} = \sqrt{\left(\frac{8 \times 8.314 \times 10^7 \times 30.4 \times 7}{22}\right)}$
-
- $$= 8.028 \times 10^4 \text{ cm sec}^{-1}$$
-
101. Given,
- $n = 10^{23}$
- ,
- $m = 10^{-22} \text{ g}$
- ,
- $V = 1 \text{ litre} = 10^3 \text{ cm}^3$
-
- $u_{rms} = 10^5 \text{ cm sec}^{-1}$
-
- $$\therefore PV = \frac{1}{3} m n u_{rms}^2$$
- $$\therefore P \times 10^3 = \frac{1}{3} \times 10^{-22} \times 10^{23} \times (10^5)^2$$
- $$\therefore P = 3.3 \times 10^7 \text{ dyne cm}^{-2}$$
-
- 102.
- $T = 27 + 273 = 300 \text{ K}$
- ,
- $R = 8.314 \times 10^7 \text{ erg}$
-
- u_{rms}
- for
- $CH_4 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 10^7 \times 300}{16}\right)}$
-
- $$= 6.84 \times 10^4 \text{ cm sec}^{-1}$$
- Now,
- $\text{K.E./mol } CH_4 = \frac{1}{2} M u^2 = \frac{1}{2} \times 16 \times (6.84 \times 10^4)^2$
-
- $$= 374.28 \times 10^8 \text{ erg mol}^{-1}$$
- $$\therefore \text{K.E. for } \frac{1}{2} \text{ mole } CH_4 = \frac{374.28 \times 10^8}{2} \text{ erg}$$
- $$= \frac{374.28 \times 10^8}{2 \times 10^7} \text{ joule}$$
- $$= 1871.42 \text{ joule}$$

Average kinetic energy

$$= \frac{\text{K.E./mol}}{\text{Av. No.}} = \frac{374.28 \times 10^8}{6.023 \times 10^{23}} = 62.14 \times 10^{-15} \text{ erg}$$

$$= 62.14 \times 10^{-22} \text{ joule}$$

$$103. \text{ Average kinetic energy} = \frac{\text{K.E./mol}}{\text{Av. No.}} = \frac{3RT}{2 \times N} = \frac{3}{2} kT$$

$$\therefore k = \frac{5.621 \times 10^{-14} \times 2}{3 \times 273} \quad (\because T = 273 \text{ K})$$

$$= 1.372 \times 10^{-16} \text{ erg molecule}^{-1} \text{ K}$$

Now Avogadro's no.

$$= \frac{R}{k} = \frac{8.314 \times 10^7}{1.372 \times 10^{-16}} = 6.059 \times 10^{23}$$

$$104. \text{ Given, } P = 7.57 \times 10^3 \text{ Nm}^{-2}, \quad V = 1 \text{ litre} = 10^{-3} \text{ m}^3$$

$$R = 8.314 \text{ J}, \quad n = \frac{2 \times 10^{21}}{6.023 \times 10^{23}} \text{ mole}$$

Using

$$PV = nRT$$

$$7.57 \times 10^3 \times 10^{-3} = \frac{2 \times 10^{21}}{6.023 \times 10^{23}} \times 8.314 \times T$$

$$\therefore T = 274.2 \text{ K}$$

$$\therefore u_{\text{rms}} = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3 \times 8.314 \times 274.2}{28 \times 10^{-3}}\right)} \quad (M \text{ in kg})$$

$$= 494.22 \text{ m sec}^{-1}$$

Now,

$$\frac{u_{\text{MP}}}{u_{\text{rms}}} = 0.82$$

 $\therefore$

$$u_{\text{MP}} = 405.26 \text{ m sec}^{-1}$$

105. Let the u_{rms} of He and SO_2 , be u_1 and u_2 respectively,

$$(i) \text{ For He: } u_1 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3RT}{4}\right)}$$

$$\text{For } \text{SO}_2: u_2 = \sqrt{\left(\frac{3RT}{M}\right)} = \sqrt{\left(\frac{3RT}{64}\right)} \quad (\text{temp. is same})$$

$$\therefore \frac{u_1}{u_2} = 4$$

$$(ii) \text{ Given, } u_{\text{rms}} \text{ of } \text{SO}_2 = \frac{1}{2} u_{\text{rms}} \text{ of He}$$

$$\therefore \sqrt{\left(\frac{3RT}{64}\right)} = \frac{1}{2} \sqrt{\left(\frac{3RT}{4}\right)}$$

(T = 300 K for He)

$$\therefore T = 1200 \text{ K}$$

(iii) Since speed is independent of P and V terms and thus no effect on speed by changing volume.

(iv) Since u_{rms} is independent of no. of molecules and thus, no effect on speed by changing no. of molecules.106. Let mass of mist particle be m, then K.E. of this particle = $\frac{1}{2} mu^2$, where u is its rms velocity.

$$\text{Also K.E. per molecule} = \frac{3RT}{2 \times N}$$

$$\text{Therefore, } \frac{1}{2} mu^2 = \frac{3RT}{2 \times N}$$

$$u = \sqrt{\left[3 \frac{R}{N} \times \frac{T}{m}\right]}$$

$$\therefore m = 10^{-12} \text{ g}; \quad R = 8.314 \times 10^7 \text{ erg}, \quad T = 300 \text{ K}$$

$$\therefore u = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{6.023 \times 10^{23} \times 10^{-12}}} = 0.35 \text{ cm sec}^{-1}$$

$$107. \text{ For } \text{H}_2: u_{\text{AV}} = \sqrt{\left(\frac{8R \times 300}{\pi \times 2}\right)}$$

(\because T = 300 K and molar mass = 2)

$$\text{For } \text{C}_2\text{H}_6: u_{\text{AV}} = \sqrt{\left(\frac{8R \times 900}{\pi \times 30}\right)}$$

(\because T = 900 K and molar mass = 30)

$$\therefore \frac{u_{\text{AVH}_2}}{u_{\text{AVC}_2\text{H}_6}} = \sqrt{\left(\frac{300 \times 30}{900 \times 2}\right)} = 2.237:1$$

$$108. (a) \text{ Volume of 1 molecule} = \frac{4}{3} \pi r^3 \text{ (spherical shape)}$$

(\because r = 150 pm = 150 \times 10^{-10} cm)

$$\therefore \text{Volume of 1 molecule} = \frac{4}{3} \times \frac{22}{7} \times [150 \times 10^{-10}]^3$$

$$(V_1) = 1.41 \times 10^{-23} \text{ cm}^3$$

(b) Thus, volume occupied by N molecules = N \times V_1

$$= 6.023 \times 10^{23} \times 1.41 \times 10^{-23} = 8.49 \text{ cm}^3 \text{ per mol}$$

Also volume of 1 mole of N_2 = 22400 cm³ at STP

Thus, empty space = 22400 - 8.49 = 22391.51

or % empty space = $\frac{22391.51}{22400} \times 100 = 99.96\%$

(c) 99.96% is empty space and this accounts that most of the space in container is empty in which a molecule can move. Also it suggests for compressibility of gases to higher extent.

109.

$$PV = nRT \quad \dots(1) \quad \text{for ideal gas}$$

$$PV^2 = K \quad \dots(2) \quad \text{additional law}$$

or

$$PV = \frac{K}{V} \quad \dots(3)$$

By Eqs. (1) and (3)

$$\therefore \frac{K}{V} = nRT$$

$$\text{Initially } \frac{K}{V} = nRT$$

$$\text{Finally } \frac{K}{2V} = nRT_1$$

$$\therefore 2 = \frac{T}{T_1}$$

$$\text{or } T_1 = \frac{T}{2}$$

110. Let P, V represent pressure and volume at temperature T.

$$PV = nRT \quad \dots(1)$$

$$\text{At } V = V_0, P = \frac{P^\circ}{1 + (1)^2} = \frac{P^\circ}{2}$$

$$\therefore P = \frac{P^\circ}{1 + \left(\frac{V}{V_0}\right)^2}$$

$$\therefore \text{By Eq. (1), } \frac{P^\circ}{2} \times V_0 = nRT$$

$$\therefore T = \frac{P^\circ V^\circ}{2R} \quad (n=1)$$

$$111. \text{ Pressure correction} = \frac{n^2 a}{V^2} = \frac{(4.4)^2 \times 3.6}{(44)^2 \times 1 \times 1} \quad \left(n = \frac{4.4}{44}\right)$$

$$= 0.036 \text{ atm}$$

$$\text{Volume correction} = nb = \frac{4.4}{44} \times 0.04 = 0.004 \text{ litre}$$

$$112. \therefore b = 4N \times v$$

[where v is volume of 1 molecule (of steam)]

$$\therefore \text{Volume of 1 mole of steam}$$

$$= \frac{b}{4} = \frac{0.0305}{4} \text{ litre} = \frac{0.0305}{4} \times 10^3 \text{ mL} = 7.625 \text{ mL}$$

$$\text{Also, volume of 1 mole of } H_2O(l) = \frac{18}{0.958} \text{ mL}$$

$$\therefore \frac{\text{Volume of 1 mole steam}}{\text{Volume of 1 mole } H_2O} = \frac{7.625 \times 0.958}{18} = 0.4058$$

$$\therefore \text{Volume of 1 mole of steam} = 40\% \text{ of volume of 1 mole of } H_2O$$

$$113. \text{ For gaseous water, } PV = nRT$$

Thus, volume occupied by 1 mole gaseous water can be derived as ($T = 273 + 100 = 373 \text{ K}$)

$$V = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 373}{1} = 30.62 \text{ litre}$$

$$\text{Also volume of 1 mole of liquid water} = \frac{\text{mass}}{\text{density}}$$

$$= \frac{18}{0.958} = 18.79 \text{ mL} = 18.79 \times 10^{-3} \text{ litre}$$

Thus, volume percentage occupied by water molecules in gaseous state

$$= \frac{18.79 \times 10^{-3}}{30.62} \times 100 = 0.0614$$

$$\text{Therefore, percentage of free volume} = 100 - 0.0614 = 99.9386$$

$$114. \therefore 6.023 \times 10^{23} \text{ molecules of } N_2 \text{ occupy } 22400 \text{ cm}^3$$

$$\therefore \text{one molecule of } N_2 \text{ occupies } \frac{22400}{6.023 \times 10^{23}} \text{ cm}^3$$

$$\text{or volume of one molecule of } N_2 = 3.72 \times 10^{-20} \text{ cm}^3$$

Also, the average distance between two molecules = $2r$

$$\text{and } \frac{4}{3} \pi r^3 = 3.72 \times 10^{-20}$$

$$\therefore r^3 = \frac{3.72 \times 10^{-20} \times 3 \times 7}{4 \times 22}$$

$$\therefore r = 20.7 \times 10^{-8} \text{ cm}$$

$$\text{Thus, average distance} = 2 \times 20.7 \times 10^{-8}$$

$$= 41.4 \times 10^{-8} \text{ cm}$$

$$115. b = 4 \times \text{Volume occupied by the molecules in one mole of gas}$$

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

$$\therefore r = \left[\frac{3 \times 24}{16 \times (22/7) \times 6.023 \times 10^{23}} \right]^{1/3} = 1.355 \times 10^{-8} \text{ cm}$$

$$\therefore d = 2 \times r = 2 \times 1.355 \times 10^{-8} \text{ cm} = 2.71 \text{ \AA}$$

$$116. (i) \text{ The volume of sphere} = \frac{4}{3} \pi r^3$$

Thus, volume of one N_2 molecule

$$= \frac{4}{3} \times \frac{22}{7} \times (2 \times 10^{-10})^3 \text{ m}^3 = 3.35 \times 10^{-23} \text{ cm}^3$$

$$(ii) \text{ The total volume of one mole of gas at STP} = 22400 \text{ cm}^3$$

Also the volume of one mole of gas

$$= N \times \text{volume of one molecule}$$

$$= 6.023 \times 10^{23} \times 3.35 \times 10^{-23} \text{ cm}^3 = 20.2 \text{ cm}^3$$

$$\therefore \text{Empty space} = 22400 - 20.2 = 22379.8 \text{ cm}^3$$

$$\therefore \text{Percentage empty space} = \frac{22379.8}{22400} \times 100 = 99.9\%$$

[NOTE : This result clearly indicates that particles of gas occupy only a tiny fraction of the total gaseous volume.]

$$117. \text{ Given, } n = 5; V = 1 \text{ litre; } T = 47 + 273 = 320 \text{ K}$$

$$a = 3.592; \quad b = 0.0427$$

Using van der Waals' equation for n mole

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

$$\left[P + \frac{25 \times 3.592}{1}\right][1 - 5 \times 0.0427] = 5 \times 0.0821 \times 320$$

$$\therefore P = 77.218 \text{ atm}$$

Also, if gas behaves ideally, then $PV = nRT$

$$P \times 1 = 5 \times 0.0821 \times 320 = 131.36 \text{ atm}$$

$$118. \text{ For 1 mole : } \left[P + \frac{a}{V^2}\right][V - b] = RT$$

$$\text{if } b \text{ is negligible, } P = \frac{RT}{V} - \frac{a}{V^2}$$

$$\text{or } PV^2 - RTV + a = 0$$

The equation is quadratic in V , thus

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

Since, V has one value at given P and T , thus numerical value of discriminant = 0

$$\text{or } R^2 T^2 = 4aP$$

$$\therefore P = \frac{R^2 T^2}{4a} = \frac{(0.0821)^2 \times (273)^2}{4 \times 3.592} = 34.96 \text{ atm}$$

$$119. Z = \frac{PV}{RT} = 0.5$$

$$\therefore \frac{100 \times V}{0.082 \times 273} = 0.5$$

$$\therefore V = 0.112 \text{ litre}$$

Now using van der Waals' equation,

$$\left[P + \frac{a}{V^2}\right][V] = RT \quad (\because b \text{ is negligible})$$

$$\text{or } \left[P + \frac{a}{V^2} \right] = \frac{RT}{V}$$

$$\therefore \left[100 + \frac{a}{(0.112)^2} \right] = \frac{0.082 \times 273}{0.112} = 199.88$$

$$\therefore \frac{a}{(0.112)^2} = 99.88$$

$$\therefore a = 1.253 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$$

120. Compressibility factor (Z) = $\frac{PV}{nRT}$

$$Z = \frac{40 \times 0.4}{1 \times 0.0821 \times 300} = 0.65$$

Since, Z value is lesser than 1 and thus, $nRT > PV$. In order to have $Z = 1$, volume of CO_2 must have been more at same P and T or CO_2 is more compressible than ideal gas.

121. For real gas $PV = Z \cdot nRT = \frac{Z \cdot wRT}{M}$

Given compressibility factor $Z = 0.927$, $T = 273 \text{ K}$,
 $P = 100 \text{ atm}$, $V = 100 \text{ litre}$

$$\therefore 100 \times 100 = 0.927 \times \frac{w}{30} \times 0.0821 \times 273$$

$$w = 14.439 \times 10^3 \text{ g}$$

$$w = 14.439 \text{ kg}$$

122. (a) (i) $\frac{r_{(v)}}{r_{(\text{O}_2)}} = \sqrt{\frac{M_{(\text{O}_2)}}{M_{(v)}}}$

$$\therefore 1.33 = \sqrt{\frac{32}{M_{(v)}}}$$

$$\therefore M_{(v)} = 18.1$$

(ii) Molar volume at 500 K

$$(\bar{V}) = \frac{\text{Molar mass}}{\text{Density of 1 mole}} = \frac{18.1 \times 10^{-3}}{0.36}$$

$$= 50.25 \times 10^{-3} \text{ m}^3$$

(iii) Compression factor

$$(Z) = \frac{P\bar{V}}{RT} = \frac{101325 \times 50.25 \times 10^{-3}}{8.314 \times 500} = 1.225$$

[$P = 101325 \text{ Nm}^{-2} = 1 \text{ atm}$]

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

(b) Average K.E. = $\frac{3}{2} kT = \frac{3}{2} \times 1.38 \times 10^{-23} \times 1000$

$$= 2.07 \times 10^{-20} \text{ J/molecule}$$

123. van der Waals' equation for n mole of gas is

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

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

Thus, $\left[11 + \frac{2^2 a}{4^2} \right] [4 - 2 \times 0.05] = 2 \times 0.082 \times 300$

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

124. $\therefore n = \frac{PV}{RT} = \frac{1 \times 5.6}{0.0821 \times 273} = 0.25$

Also, $q = m \cdot S \cdot \Delta T = 0.25 \times C_v \times 10$

$$\therefore 12.5 = 0.25 \times C_v \times 10$$

$$\therefore C_v = 5 \text{ calorie}$$

Also, $C_p = C_v + R = 5 + 2 = 7 \text{ calorie}$

So, $\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.40$

Thus, gas is diatomic.

125. Given, $P = 50 \text{ atm}$, $V = 25 \text{ litre}$, $n = 10$

$$a = 5.46 \text{ atm litre}^2 \text{ mol}^{-2}$$
, $b = 0.031 \text{ litre mol}^{-1}$

Now van der Waals' equation for n mole of gas.

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

$$\left[50 + \frac{100 \times 5.46}{625} \right] [25 - 10 \times 0.031] = 10 \times 0.0821 \times T$$

$$\therefore T = 1529.93 \text{ K} = 1256.93^\circ \text{C}$$

126. We have, $Z = \frac{PV}{nRT}$

$$\therefore \text{Mole of } \text{N}_2 = \frac{PV}{ZRT} = \frac{800 \times 100}{1.95 \times 0.0821 \times 223} = 2240.8$$

127. Given, $T_c = 374^\circ \text{C} = 374 + 273 = 647 \text{ K}$, $P_c = 218 \text{ atm}$

$$V_c = 0.0566 \text{ litre mol}^{-1}$$

$$\therefore b = \frac{V_c}{3} = \frac{0.0566}{3} = 0.0189 \text{ litre mol}^{-1}$$

$$a = 3P_c V_c^2 = 3 \times 218 \times (0.0566)^2 = 2.095 \text{ litre}^2 \text{ atm mol}^{-2}$$

$$R = \frac{8 P_c V_c}{3 T_c} = \frac{8 \times 218 \times 0.0566}{3 \times 647} = 0.05086 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

128. According to van der Waals' equation

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

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

Multiply by V , then $PV = \frac{RTV}{(V-b)} - \frac{a}{V}$

or $PV = RT \left[\frac{V}{V-b} - \frac{a}{VRT} \right]$

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

$$\therefore \left[1 - \frac{b}{V} \right]^{-1} = 1 + \frac{b}{V} + \left(\frac{b}{V} \right)^2 + \dots$$

$$\therefore PV = RT \left[1 + \frac{b}{V} + \dots - \frac{a}{VRT} \right]$$

$$PV = RT \left[1 + \left(b - \frac{a}{RT} \right) \frac{1}{V} + \dots \right]$$

$$\therefore B = b - \frac{a}{RT}$$

129. $nA \rightleftharpoons [A]_n$

Before association	1	0
After association	$1 - \alpha$	$\frac{\alpha}{n}$

$$\therefore K_C = \frac{[A_n]}{[A]^n} = \frac{\alpha}{n \cdot V \left[\frac{1-\alpha}{V} \right]^n} = \frac{\alpha \cdot V^{n-1}}{n(1-\alpha)^n}$$

Since α is small, thus $\frac{\alpha}{n} = \frac{K_C}{V^{n-1}}$... (1)

Total mole of gas at equilibrium = $1 - \alpha + \frac{\alpha}{n}$

$$\therefore PV = \left[1 - \alpha + \frac{\alpha}{n} \right] RT$$

$$\text{or } \frac{PV}{RT} = 1 - \alpha + \frac{\alpha}{n} = \frac{n - n\alpha + \alpha}{n} = \left[1 - (n-1) \frac{\alpha}{n} \right]$$

$$\therefore \text{By Eq. (1), } \frac{PV}{RT} = \left[1 - \frac{(n-1) \cdot K_C}{V^{n-1}} \right]$$

130. For real gas: $\left[P + \frac{a}{V^2} \right] [V - b] = RT$

or $P[V - b] = RT$ (neglecting a)

$$\therefore \frac{10.1325 \times 10^6}{101325} [V_1 - b] = 0.0821 \times 273 (101325 \text{ Pa} = 1 \text{ atm})$$

$$\text{or } 100[V_1 - b] = 0.0821 \times 273 = 22.41 \quad \dots (i)$$

$$\frac{101.325 \times 10^3}{101325} [V_2 - b] = 0.0821 \times 273$$

$$\text{or } [V_2 - b] = 22.41 \quad \dots (ii)$$

$$\text{By Eq. (i), } V_1 = 0.2241 + b \quad \dots (iii)$$

$$\text{By Eq. (ii), } V_2 = 22.41 + b \quad \dots (iv)$$

$$\text{By Eqs. (iii) and (iv), } \frac{V_1}{V_2} = \frac{0.2241 + b}{22.41 + b}$$

$$\frac{0.011075 V_2}{V_2} = \frac{0.2241 + b}{22.41 + b}$$

$$(V_1 = 0.011075 V_2 \text{ is given})$$

$$\therefore b = 0.024 \text{ litre mol}^{-1} = 24 \text{ cm}^3 \text{ mol}^{-1}$$

$$\therefore b = 4N \times v = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \pi r^3$$

$$\text{or } 24 = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times r^3$$

$$\therefore r = 1.33 \times 10^{-8} \text{ cm}$$

131. (a) Given $P(V - b) = nRT$
 $1 \times (25 - b) = 1 \times 0.0821 \times 273$
 $(\because V = 25 \text{ dm}^3 = 25 \text{ litre})$

$$\therefore b = 2.586 \text{ litre}$$

Also, diameter of molecule $d = 2r$

We have $b = 4 \times N \times \text{Volume of molecule}$
 $= 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \pi r^3$

$$\therefore 2.586 = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \times \frac{22}{7} \times \left(\frac{d}{2} \right)^3$$

$$\therefore d = 1.270 \times 10^{-8} \text{ cm}$$

(b) Given $P(V - b) = nRT$, $PV - Pb = nRT$

$$\frac{PV}{nRT} - \frac{Pb}{nRT} = 1$$

$$\text{or } Z - \frac{Pb}{nRT} = 1$$

$$(\because \frac{PV}{nRT} = Z, \text{ i.e., compressibility factor})$$

$$\text{or } Z = 1 + \frac{Pb}{nRT} = 1 + \frac{1 \times 2.586}{1 \times 0.0821 \times 273} = 1.115$$

132. $T_C = \frac{8a}{27Rb}$ and $P_C = \frac{a}{27b^2}$

$$\therefore \frac{T_C}{P_C} = \frac{8b}{R} \quad \text{or} \quad b = \frac{RT_C}{8P_C}$$

$$\therefore b = \frac{0.0821 \times 303}{8 \times 72} = 0.043 \text{ litre mol}^{-1}$$

$$a = 27P_C \times b^2 = 27 \times 72 \times (0.043)^2 = 3.59 \text{ litre}^2 \text{ atm mol}^{-2}$$

133. For O_2 : $T_1 = \frac{T}{T_{C1}} = \frac{300}{155}$

For N_2 : $T_2 = \frac{T}{T_{C2}} = \frac{300}{126}$

$$\therefore \frac{T_1}{T_2} = \frac{126}{155} = 0.812$$

134. According to law of corresponding state

$$\left[P_r + \frac{3}{V_r^2} \right] [3V_r - 1] = 8RT_r$$

$$\left[P_r + \frac{3}{(0.4)^2} \right] [3 \times 0.4 - 1] = 8 \times 0.7277$$

$$\therefore P_r = 10.350$$

135. Inversion temperature,

$$T_i = \frac{2a}{R \cdot b} = \frac{2 \times 0.246}{0.0821 \times 0.0267} = 224.4 \text{ K}$$

Boyle temperature,

$$T_b = \frac{a}{R \cdot b} = \frac{0.246}{0.0821 \times 0.0267} = 112.2 \text{ K}$$

136. Let pressure of gas left in vessel after I operation be P_1 . Let n_1 mole are removed from vessel after I operation. Let n mole were present initially.

Thus, Initial state $PV = nRT$... (i)

$$\therefore P_1 V = (n - n_1) RT \quad \dots (ii)$$

$$P_1 V = nRT - n_1 RT$$

$$P_1 V = PV - n_1 RT \quad \dots (iii)$$

The n_1 mole taken out has volume v at pressure P_1

Thus, $P_1 v = n_1 RT$... (iv)

By Eqs. (iii) and (iv), $P_1 V = PV - P_1 v$

or $P_1 = P \left[\frac{V}{V + v} \right] \quad \dots (v)$

Similarly, for II operation: $P_2 = P_1 \left[\frac{V}{V + v} \right] = P \left[\frac{V}{V + v} \right]^2$

Thus, for n operations $P_n = P \left[\frac{V}{V + v} \right]^n$

137. For real gases, van der Waals' equation for one mole is:

$$\left[P + \frac{a}{V_m^2} \right] [V_m - b] = RT$$

$$\text{or } PV_m - Pb + \frac{a}{V_m} - \frac{ab}{V_m^2} = RT \quad \dots(1)$$

For intercept of PV_m vs. P graph at y -axis, $P = 0$ and thus, $v_m \rightarrow \infty$. Thus neglecting $\frac{a}{V_m}$ and $\frac{ab}{V_m^2}$ terms in Eq. (1)

$$\text{or } PV_m = Pb + RT \quad \dots(2)$$

Thus, a graph between PV_m vs. P will lead to an intercept RT as Eq. (2) represents a straight line equation ($y = mx + c$).

138.

$$\text{Mole of He} = \frac{1}{4}$$

$$\text{Mole of O}_2 = \frac{4}{32} = \frac{1}{8}$$

∴

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

For O₂ :

$$1000 = \sqrt{\frac{3 \times 8.314 \times T}{32 \times 10^{-3}}}$$

$$[M_{\text{O}_2} = 32 \times 10^{-3} \text{ kg}]$$

∴

$$T_{\text{O}_2} = 1283.0 \text{ K}$$

For He :

$$1000 = \sqrt{\frac{3 \times 8.314 \times T}{4 \times 10^{-3}}}$$

$$[M_{\text{He}} = 4 \times 10^{-3} \text{ kg}]$$

$$T_{\text{He}} = 160.37 \text{ K}$$

$$\therefore \text{K.E. per } \frac{1}{4} \text{ mole He} = \frac{3}{2} \times \frac{1}{4} \times 8.314 \times 160.3 = 500 \text{ J}$$

$$\text{K.E. per } \frac{1}{8} \text{ mole O}_2 = \frac{3}{2} \times \frac{1}{8} \times 8.314 \times 1283.0 = 2000.036 \text{ J}$$

At thermal equilibrium temperature (T) becomes constant as O₂ molecules provide heat energy to He molecules.

Heat given is expressed as $n \times c_v \times \Delta T$

$$\left(c_v = \frac{3}{2}R \text{ for He and } \frac{5}{2}R \text{ for O}_2 \right)$$

Heat given by O₂ = Heat taken up by H₂

$$\frac{1}{8} \times \frac{5}{2} R \times (1283 - T) = \frac{1}{4} \times \frac{3}{2} R \times (T - 160.37)$$

$$\therefore 5(1283 - T) = 2 \times 3(T - 160.37)$$

$$6415 - 5T = 6T - 962.22$$

$$\therefore T = 670.7 \text{ K}$$

$$\text{Thus, } u_{\text{rms}} \text{ for O}_2 = \sqrt{\frac{3 \times 8.314 \times 670.7}{32 \times 10^{-3}}} = 723 \text{ m/s}$$

$$u_{\text{rms}} \text{ for He} = \sqrt{\frac{3 \times 8.314 \times 670.7}{4 \times 10^{-3}}} = 2045 \text{ m/s}$$

139. According to Maxwell's molecular speed distribution :

(a) The number of molecules of a given gas having their speed near to u_{MP} increases with temperature.

(b) The number of molecules having their speed near to u_{MP} decreases with increase in molar mass for gases at constant temperature.

(c) The number of molecules having their speed near to u_{MP} increases with increase in u_{MP} .

Also, $n \propto u_{MP}$

$$\therefore n_1 \propto \sqrt{\frac{2RT_1}{M_1}}, \quad n_2 \propto \sqrt{\frac{2RT_2}{M_2}}$$

$$\therefore M_1 = M_2$$

$$\therefore \frac{n_1}{n_2} = \sqrt{\frac{T_1}{T_2}}$$

$$T_2 = 300, \quad n_1 = \frac{n_2}{2}$$

$$\therefore \frac{1}{2} = \sqrt{\frac{T}{300}} \quad \therefore T = 75 \text{ K}$$

140. According to Maxwell's molecular speed distribution :

$$\frac{n_g}{\sum n_g} \propto \frac{1}{u_{\text{rms}}}$$

$$\therefore u_{\text{rms}} \propto \frac{\sum n_g}{n_g} \propto \frac{N}{n_g} \quad (\because 1 \text{ mole of both gases})$$

$$u_{\text{rms Ar}} \propto \frac{N}{n_{\text{Ar}}}, \quad u_{\text{rms He}} \propto \frac{N}{n_{\text{He}}}$$

$$\therefore \frac{n_{\text{He}}}{n_{\text{Ar}}} = \frac{u_{\text{rms Ar}}}{u_{\text{rms He}}} = \frac{467}{1477} = 0.316$$

● SINGLE INTEGER ANSWER PROBLEMS ●

1. A container having 3 mole of ideal gas occupies 60 litres at pressure P and temperature T . If 0.1 mole of gas is introduced at same P and T in container the change in volume will be litre.
2. An ideal gas on heating from 100 K to 109 K shows an increase by $a\%$ in its volume at constant P . The value of a is
3. The ratio of inversion temperature and Boyle's temperature for a real gas is
4. The specific heat of a gas are 0.125 and 0.075 cal/g. The $1/10^{\text{th}}$ value of its molar mass is
5. A bulb is having ideal gas at 27°C . On heating the bulb to 227°C , 2 litre of gas measured at 227°C is expelled out. The volume of bulb in litre is
6. The mass of molecule A is twice the mass of molecule B . The rms speed of A is twice the rms speed of B . If two samples of A and B contain same number of molecule, the ratio of pressure of gas samples of A and B in separate containers of equal volume is
7. Molar mass of air is 28.80 g mol^{-1} . The volume of N_2 (in mL) in 10 mL of sample of this air is
8. A cylinder containing 5 litre of O_2 at 25°C was leaking. When the leakage was detected and checked, the pressure inside cylinder was reduced from 8 atm to 2 atm. The ratio of mass of O_2 initially present to that left after leakage is equal to
9. 16 mL of He gas effuses through a pin hole in 4 sec from a container having P_{He} equal to 1 atm. If same container is filled with CH_4 having pressure 2 atm, how much volume (in mL) of CH_4 will be leaked through same pin hole in 2 sec?
10. U_{rms} of CH_4 at $T \text{ K}$ is 6 times of U_{mp} of SO_2 at $T_1 \text{ K}$. The temperature of CH_4 gas is times of SO_2 .
11. Root mean square speed of a gas is 5 ms^{-1} . If some molecules out of 10 molecules in all are moving with 7 ms^{-1} and rest all the molecules moving with 3 ms^{-1} , then number of molecules moving with higher speed is
12. A metallic carbonyl $M(\text{CO})_X$ is in gaseous state. The rate of diffusion of CH_4 is 3.31 time faster than this gas under identical conditions. If at. mass of metal is 63.29, the closest integer value of X is
13. The ratio of rate of diffusion of He (at 4 atm) and CH_4 (1 atm) through same pin hole at constant temperature is
14. 5 mL of a liquid [$V.P. = 8 \text{ cm}$ at 400 K] having density 0.02 g/mL is placed in a container of 4 litre. It is connected to another empty container of 4 litre at 400 K . The resultant pressure of liquid shown is
15. A gas having molecular formula O_n . If its vapour density is 24. The value of n is
16. The percentage decrease in volume of gas at constant temperature if percentage increase in pressure is 5.26, is
17. An ideal gas on heating shows a rise in temperature by 8% at constant pressure. The % increase in volume of gas is
18. The density of vapours of a substance at 1 atm P and 500 K is 0.3 kg m^{-3} . The vapours effuse 0.4216 times faster than O_2 through a pin hole under identical conditions. If $R = 0.08 \text{ litre atm K}^{-1} \text{ mol}^{-1}$. The molar volume of gas is $a \times 10^2 \text{ litre}$. The value of a is
19. What mass of N_2 should be mixed with 11g of CO to give a mean molar mass of mixture equal to 36 ?
20. A flask of capacity 5 litre containing air is heated from 27°C to 227°C . The volume (in litre) of air left in flask on heating is
21. A flask of capacity 10 litre containing air is heated from 27°C to 227°C . The ratio of mole of air present at 27°C to mole present at 227°C is
22. $w_1 \text{ g}$ of gas A and $w_2 \text{ g}$ of gas B shows a mixture of molar mass 72. This $(w_1 + w_2) \text{ g}$ mixture is placed in a container of volume V litre at 1 atm and 300 K . The density of mixture at these conditions is kg m^{-3} . ($R = 0.08 \text{ litre-atm K}^{-1} \text{ mol}^{-1}$)
23. A certain quantity of gas occupies 960 litre when collected over water at 300 K and 760 mm pressure. However the same quantity of dry gas occupies 608 litre at 2 atm and 400 K . The number of mole of water vapours present in wet gas is ($R = 0.08 \text{ litre atm K}^{-1} \text{ mol}^{-1}$).... .
24. 0.75 mole of solid A_4 and 2 mole of gaseous O_2 are heated to react completely in a sealed bottle to produce gaseous compound $A_3\text{O}_n$. After the compound is formed, the vessel is brought to initial temperature, the pressure is found to half of initial pressure. The value of n is
25. A graph is plotted for a van der Waals' gas between PV_m vs P leading to an intercept of 22.16 litre-atm . The temperature of gas at which these observations of P and V_m were made is $^\circ\text{C}$. ($R = 0.08 \text{ litre atm K}^{-1} \text{ mol}^{-1}$)
26. Two boxes A and B having their volume ratio 1 : 4 and filled with Ne are inter connected through a narrow tube of negligible volume. Box A is kept at 300 K and box B at 600 K . The ratio of mole of Ne gas in box B to box A is
27. The density of the vapours of a substance at 1 atm and 500 K is 0.36 kg m^{-3} . If molar mass of gas is 18 g mol^{-1} , the molar volume of gas is $5 \times 10^4 \text{ m}^3$. What is the value of a ?

28. The root mean square speed of the molecules of diatomic gas is u at temperature T . On increasing the temperature to $2T$, the molecules are dissociated. At this time u_{rms} of the atoms is au . The value of a is
29. The u_{rms} of the molecules of a gas of density 4 kg m^{-3} and pressure $1.2 \times 10^5 \text{ Nm}^{-2}$ is $3 \times 10^4 \text{ cm/sec}$. The value of a is
30. One litre of N_2 and $7/8$ litre of O_2 under identical conditions of P and T are mixed. The mass ratio of N_2 and O_2 is
31. Density of a gas is found 5.46 g/L at 27°C and 2 atm pressure. What will be its density at STP in g/L ?
32. A balloon is filled with 2.4×10^{-3} mole of He at 27°C and 80 mm pressure. An additional amount of He (1.2×10^{-3} mole) is added at the same temperature showing a rise in volume by 50% . The final pressure of gas in balloon in cm is
33. A given sample of gas occupies 40.5 mL at a certain P and T . If mass of the gas is doubled and absolute temperature is lowered to $T/3$ but pressure increases to $9P$, the volume occupied by gas will be mL .
34. The composition of air is $20\% \text{ O}_2$ and $80\% \text{ N}_2$ by volume. If 10 litre of air is placed at 24.9584 atm and 304 K , the mole of O_2 present to closest integer values are....
35. A closed container of volume 0.02 m^3 consists 28 g of mixture of neon and argon at temperature 27°C and pressure $1 \times 10^5 \text{ Nm}^{-2}$. If atomic mass of Ne and Ar are 20 and 40 respectively, the mass of Ne in mixture (in g) is
36. If pressure of gases at sun is $1.4 \times 10^9 \text{ atm}$, density is 1.4 g/mL and average molar mass of gaseous mixture is 2 , the temperature of sun is $2.4 \times 10^a \text{ K}$. The value of a is
37. A flask contains a mixture of N_2 and CO_2 at 1.5 atm and 27°C . If CO_2 is removed the pressure falls to 0.5 atm and the mass of the flask drops by 22 g . The mass of N_2 in g in flask is
38. If $T_A : T_B$ is $2 : 1$, the ratio of u_{rms} of two gases A and B is $2\sqrt{2} : 1$ respectively. What would be the ratio of the rate of diffusion of two gases A and B under same P and T ?
39. A mixture of H_2 and O_2 in $2:1$ volume ratio is allowed to diffuse through a porous partition. The composition ratio of $\text{H}_2 : \text{O}_2$ coming out initially would be
40. A cylinder containing 5.0 litre O_2 at 25°C was leaking. When the balloon leakage was detected and stopped, there was a change in the pressure of the gas from 3.0 atm to 2.235 atm . The massing of O_2 leaked out is
41. By how many times the absolute temperature of a gas would increase when u_{rms} of a gas in a container of fixed volume is increased from $5 \times 10^4 \text{ cm sec}^{-1}$ to $10 \times 10^4 \text{ cm sec}^{-1}$?
42. The ratio of pressure of a gas when u_{rms} of a gas in a container is increased from $5 \times 10^4 \text{ cm sec}^{-1}$ to $10 \times 10^4 \text{ cm sec}^{-1}$.
43. 11.2 litre of a gas at NTP requires 40 cal heat to raise its temperature from 0°C to 10°C . The specific heat at constant volume of gas in calories is
44. The ratio of root mean square speed of He and SO_2 gases placed in two containers of identical volume at same P and T is
45. A vessel having movable piston containers has 6.0 mole of a gas at 8.0 atm pressure and volume 5.0 litre . 1.5 mole of gas are withdrawn as well as piston is pulled isothermally onwards to make volume of vessel 10.0 litre . The final pressure of gas will be
46. The isothermal compressibility factor ' α ' for an ideal gas at 0.25 atm pressure is
47. The mixture of one mole of monoatomic gas and one mole diatomic gas has molar specific heat at constant volume (in cal) equal to
48. The heat used in calorie in doing work during the heating of 1 mole diatomic gas at constant pressure in order to increase the temperature of gas through 1°C .
49. At 400 K , the root mean square speed of a gas (molar mass = 40) is equal to the most probable speed of gas y at 60 K . The molar mass of the gas y is (IIT 2009)
50. To an evacuated vessel with movable piston under external pressure of 1 atm , 0.1 mol of He and 1.0 mol of an unknown compound (vapour pressure 0.68 atm at 0°C) are introduced. Considering the ideal gas behaviour, the total volume (in litre) of the gases at 0°C is close to (IIT 2011)

ANSWERS

- | | | | | | | | | | | | |
|-----------|---|-----------|----------|-----------|----------|-----------|-----------|-----------|-----------|----------|-----------|
| 1. Two | 2. Nine | 3. Two | 4. Four | 5. Three | 6. Eight | 7. Eight | 8. Four | 9. Eight | 10. Six | 11. Four | 12. Four |
| 13. Eight | 14. Eight | 15. Three | 16. Five | 17. Eight | 18. Six | 19. Seven | 20. Five | 21. Two | 22. Three | 23. Two | 24. Four |
| 25. Four | 26. Two | 27. Three | 28. Two | 29. Four | 30. One | 31. Three | 32. Eight | 33. Three | 34. Two | 35. Four | 36. Seven |
| 37. Seven | 38. Two | 39. Eight | 40. Five | 41. Four | 42. One | 43. Eight | 44. One | 45. Four | 46. Four | 47. Four | 48. Two |
| Four | 50. Seven (Saturated vapours do not obey gas laws except Dalton's law of vapour pressure) | | | | | | | | | | |

OBJECTIVE PROBLEMS (One Answer Correct)

- If X_M , X_P and X_V are mole fraction, pressure fraction and volume fraction respectively of a gaseous mixture, then :
 - $X_M = \frac{1}{X_P} = \frac{1}{X_V}$
 - $\frac{1}{X_M} = X_P = \frac{1}{X_V}$
 - $X_M = X_P = X_V$
 - $\frac{1}{X_M} = \frac{1}{X_P} = \frac{1}{X_V}$
- Virial equation is :

$$PV_M = RT \left[A + \frac{B}{V_M} + \frac{C}{V_M^2} + \dots \right]$$
 where A , B , C are first, second, third virial coefficient respectively. For an ideal gases:
 - A = unity and B , C are zero
 - A , B , C are all equal to unity
 - A is dependent of temperature
 - All A , B , C depend on temperature
- Which of the following is intensive property?
 - P
 - V
 - Mole
 - T
- Which one is not correct for gaseous state obeying van der Waals' equation ?
 - Compressibility factor at critical temperature ≈ 0.375
 - For a gas if van der Waals' constant $a = 0$, $T_C = 0$
 - Ideal gases do not have critical temperature
 - Gaseous molecules showing H-bonding show minimum deviations from $Z \approx 0.375$
- One mole of a gas is present in a vessel at STP. The volume of container in which neither of the gas molecule is present is :
 - 22.4 litre
 - 2.24 litre
 - 2.24×10^{-1} litre
 - 22.3776 litre
- The compressibility factor for definite mass of a van der Waals' gas at 0°C and 100 atmosphere is found to be 0.5. Assuming the volume of gas molecules negligible, the van der Waals' constant ' a ' for a gas is :
 - $1.256 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$
 - $0.256 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$
 - $2.256 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$
 - $0.0256 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$
- The pressure exerted by 1 mole of CO_2 at 273 K, is 34.98 atm. Assuming that volume occupied by CO_2 molecules is negligible, the value of van der Waals' constant for attraction of CO_2 gas is :
 - $3.59 \text{ dm}^6 \text{ atm mol}^{-2}$
 - $2.59 \text{ dm}^6 \text{ atm mol}^{-2}$
 - $1.25 \text{ dm}^6 \text{ atm mol}^{-2}$
 - $1.59 \text{ dm}^6 \text{ atm mol}^{-2}$
- Relative humidity of air is 60% and the saturation vapour pressure of water vapour in air is 3.6 kPa. The mass of water vapours present in 2 litre air at 300 K is :
 - 52 g
 - 31.2 g
 - 26 g
 - 5.2 g
- A 3 : 2 molar mixture of N_2 and CO is present in a vessel at 500 bar pressure. Due to hole in the vessel, the gas mixture leaks out. The composition of mixture effusing out initially is :
 - $n_{\text{N}_2} : n_{\text{CO}} :: 1 : 2$
 - $n_{\text{N}_2} : n_{\text{CO}} :: 6 : 1$
 - $n_{\text{CO}} : n_{\text{N}_2} :: 1 : 2$
 - $n_{\text{CO}} : n_{\text{N}_2} :: 2 : 3$
- Number of N_2 molecules present in 1 litre vessel at NTP when compressibility factor is 1.2 is :
 - 2.23×10^{24}
 - 2.23×10^{22}
 - 2.7×10^{22}
 - 2.7×10^{24}
- Select the correct statement :
 - A mixture of ideal gases is cooled up to liquid the temperature (4.22 K) to form ideal solution.
 - Ideal gas can be liquefied on applying pressure and lowering temperature.
 - Kinetic energy of a gas is zero at 0°C .
 - Ideal gas on subjecting to Joule-Thomson effect do not show cooling on account of absence of molecular forces of attraction.
- Select the incorrect statement :
 - Compressibility factor for an ideal gas is unity.
 - A real gas approaches ideal gas nature at high temperature and low pressure.
 - The compressibility factor $Z > 1$, then for a gas when repulsive forces predominate.
 - van der Waals' constant ' a ' for NH_3 is smaller than N_2 .
- 0.44 g dry ice is placed in an evacuated chamber of 5 litre at 27°C . The pressure inside the vessel when whole dry ice has been evaporated to gaseous state is:
 - 0.49 atm
 - 0.049 atm
 - 4.9×10^{-3} atm
 - 4.9 atm
- An oxide of nitrogen has density 1.33 g/litre at 764 mm Hg and 150°C . The oxide of nitrogen is:
 - N_2O_5
 - NO_2
 - N_2O
 - NO
- If P_g and P_v are partial pressure of H_2O_v and saturated vapour pressure of H_2O_v respectively, than % relative humidity is given by:
 - $\frac{P_v}{P_g} \times 100$
 - $\frac{P_g}{P_v} \times 100$
 - $\frac{P_g + P_v}{P} \times 100$
 - $\frac{P_g - P_v}{P_g} \times 100$

16. A graph plotted between Pd vs. P where P is pressure of C_2H_6 gas (assume ideal gas) and d is its density in g/L at particular temperature $\left[\frac{dPd}{dP}\right] = 20$ when $P = 8.21$ atm, the temperature of gas will be :
 (a) 400 K (b) 1200 K
 (c) 300 K (d) 600 K
17. At low pressure when b is negligible for a van der Waals' gas $RT = 2\sqrt{aP}$, then volume occupied by gas is :
 (a) $\frac{RT}{2P}$ (b) $\frac{2RT}{P}$
 (c) $\frac{2P}{RT}$ (d) $\frac{P}{RT}$
18. The pressure exerted by sodium vapours in a 2 litre container is 50 bar at 1000°C . The number of atoms of sodium in the container is :
 (a) 5.76×10^{16} (b) 5.76×10^{23}
 (c) 5.76×10^{17} (d) 5.76×10^{19}
19. The quantity $\frac{PV}{kT}$, where k represents Boltzmann's constant represents :
 (a) Number of mole of gas
 (b) Number of molecules of gas
 (c) Mass of gas
 (d) K.E./molecule of gas
20. A mixture containing Ne and Ar in a vessel at 250 K has a total translational kinetic energy = 3 kJ. The total mass of mixture is 30g. What is the mass % of Ar in mixture ?
 (a) 28.3 (b) 71.7
 (c) 50.3 (d) 30.2
21. An electric lamp is filled with an ideal gas having density 0.75 kg/m^3 and pressure $4 \times 10^4 \text{ Pa}$. On switching on the lamp, the temperature of gas molecules increases so that new pressure becomes $9 \times 10^4 \text{ Pa}$. The increase in u_{rms} of gas molecules in m/sec. is :
 (a) 200 (b) 300
 (c) 100 (d) 400
22. One mole of a monoatomic gas $\left(\gamma = \frac{5}{3}\right)$ and one mole of a diatomic gas $\left(\gamma = \frac{7}{5}\right)$ are mixed in a vessel. The value of γ for the mixture is :
 (a) 1.5 (b) 3.06
 (c) 1.53 (d) 1.43
23. At 10°C the density of a fixed mass of an ideal gas divided by its pressure is X . At 110°C , this ratio would be :
 (a) $\frac{10x}{110}$ (b) $\frac{283x}{383}$
 (c) x (d) $\frac{383}{283}x$
24. The no. of atoms of a triatomic gas in 0.1 mol is :
 (a) 1.8×10^{22} (b) 6.02×10^{23}
 (c) 1.8×10^{23} (d) 3.6×10^{23}
25. 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 :
 (a) $1/3$ (b) $1/2$
 (c) $2/3$ (d) $\frac{1}{3} \times \frac{273}{298}$
26. The temperature at which a real gas obeys the ideal gas laws over a wide range of pressure is :
 (a) Critical temperature
 (b) Boyle's temperature
 (c) Inversion temperature
 (d) Reduced temperature
27. The ratio of root mean square speed to average speed of a gas molecule at a particular temperature is :
 (a) 1.886 (b) 1.086
 (c) 0.9213 (d) 1.426
28. Helium atom is two times heavier than a hydrogen molecule. At 298K, the average kinetic energy of a helium atom is :
 (a) Two times of a H_2 molecule
 (b) Same as of H_2 molecule
 (c) Four times of a H_2 molecule
 (d) $1/2$ of H_2 molecule
29. Equal masses of methane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is :
 (a) $1/2$ (b) $8/9$
 (c) $1/9$ (d) $16/17$
30. The value of van der Waals' constant 'a' for the gases O_2 , N_2 , NH_3 and CH_4 are 1.360, 1.390, 4.170 and $2.253 \text{ L}^2 \text{ atm mol}^{-2}$ respectively. The gas which can most easily be liquefied is :
 (a) O_2 (b) N_2
 (c) NH_3 (d) CH_4
31. A liquid is in equilibrium with its vapours at its boiling point. On the average, the molecules in the two phases have equal :
 (a) inter-molecular forces
 (b) potential energy
 (c) kinetic energy
 (d) total energy
32. Rate of diffusion of a gas is :
 (a) directly proportional to its density
 (b) directly proportional to its molar mass
 (c) directly proportional to the square root of its molar mass
 (d) inversely proportional to the square root of its molar mass

33. The average speed of an ideal gas molecule at 27°C is 0.3 m/s . The average speed at 927°C will be :
 (a) 0.6 m/s (b) 0.3 m/s
 (c) 0.9 m/s (d) 3.0 m/s
34. In van der Waals' equation of state for a non-ideal gas, the term that accounts for intermolecular forces is :
 (a) $(V - b)$ (b) RT
 (c) $\left(P + \frac{a}{V^2}\right)$ (d) $(RT)^{-1}$
35. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends. The white ammonium chloride ring first formed will be :
 (a) at the centre of the tube
 (b) near the hydrogen chloride bottle
 (c) near the ammonia bottle
 (d) throughout the length of the tube
36. The density of neon will be highest at :
 (a) STP (b) 0°C , 2 atm
 (c) 273°C , 1 atm (d) 273°C , 2 atm
37. The rate of diffusion of methane at a given temperature is twice that of a gas X . The molar mass of X is :
 (a) 64.0 (b) 32.0
 (c) 4.0 (d) 8.0
38. According to the kinetic theory of gases for a diatomic molecule :
 (a) the pressure exerted by the gas is proportional to the root mean square speed of the molecule
 (b) the pressure exerted by the gas is proportional to the mean speed of the molecule
 (c) the root mean square speed of the molecule is inversely proportional of the temperature
 (d) the mean translational kinetic energy of the molecule is proportional to the absolute temperature
39. At constant volume, for a fixed number of mole of a gas, the pressure of the gas increases with rise of temperature due to :
 (a) increase in average molecular speed
 (b) increase rate of collisions amongst molecules
 (c) increase in molecular attraction
 (d) decrease in mean free path
40. Equal masses of ethane and hydrogen are mixed in an empty container at 25°C . The fraction of the total pressure exerted by hydrogen is :
 (a) $1 : 1$ (b) $1 : 2$
 (c) $1 : 16$ (d) $15 : 16$
41. The van der Waals' constant ' a ' in $\text{L}^2\text{ atm mol}^{-2}$ with gases (not reported in order are given in list A and B.)
- | List A | List B |
|--|-------------|
| (1) $\text{C}_6\text{H}_6(g)$ | (a) 0.217 |
| (2) $\text{C}_6\text{H}_5\text{CH}_3(g)$ | (b) 5.464 |
- (3) $\text{Ne}(g)$ (c) 18.00
 (4) $\text{H}_2\text{O}(g)$ (d) 24.060
- Which one is the correct match?
 (a) 1-a, 2-d, 3-c, 4-b (b) 1-d, 2-a, 3-b, 4-c
 (c) 1-c, 2-d, 3-a, 4-b (d) 1-b, 2-c, 3-a, 4-d
42. Which of the following gas molecules has the largest mean free path ?
 (a) H_2 (b) N_2
 (c) O_2 (d) Cl_2
43. The ratio between the root mean square speed of H_2 at 50 K and that of O_2 at 800 K is :
 (a) 4 (b) 2
 (c) 1 (d) $1/4$
44. $X\text{ mL}$ of H_2 gas effuses through a hole in container in 5 seconds . The time taken for the effusion of the same volume of the gas specified below under identical conditions is :
 (a) $10\text{ s} : \text{He}$ (b) $20\text{ s} : \text{O}_2$
 (c) $25\text{ s} : \text{CO}$ (d) $55\text{ s} : \text{CO}_2$
45. The compressibility factor for an ideal gas is :
 (a) 1.5 (b) 1.0
 (c) 2.0 (d) ∞
46. The critical temperature of H_2O is higher than O_2 because the H_2O molecule has :
 (a) A fewer electron than O_2
 (b) Two covalent bond
 (c) V shape
 (d) Dipole moment
47. According to Graham's law, at a given temperature the ratio of the rates of diffusion $\frac{r_A}{r_B}$ of gases A and B are given by :
 (a) $\left(\frac{P_A}{P_B}\right)\left(\frac{M_A}{M_B}\right)^{\frac{1}{2}}$ (b) $\left(\frac{M_A}{M_B}\right)\left(\frac{P_A}{P_B}\right)^{\frac{1}{2}}$
 (c) $\left(\frac{P_A}{P_B}\right)\left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$ (d) $\left(\frac{M_A}{M_B}\right)\left(\frac{P_B}{P_A}\right)^{\frac{1}{2}}$
 (where P and M are pressures and molar masses of gases A and B respectively).
48. A gas will approach ideal behaviour at :
 (a) low temperature and low pressure
 (b) low temperature and high pressure
 (c) high temperature and low pressure
 (d) high temperature and high pressure
49. Which of these gases exhibits behaviour that deviates most significantly from that expected for an ideal gas?
- (a)

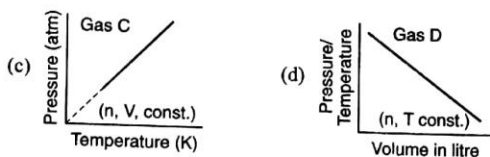
Volume (V)

Temperature (K)

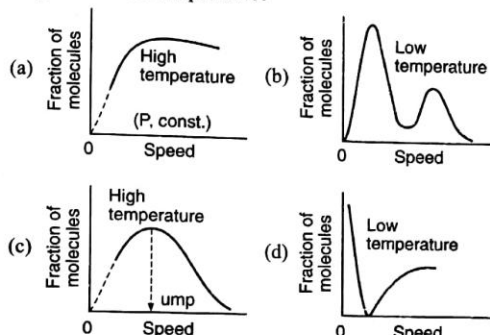
(b)

Pressure x Volume

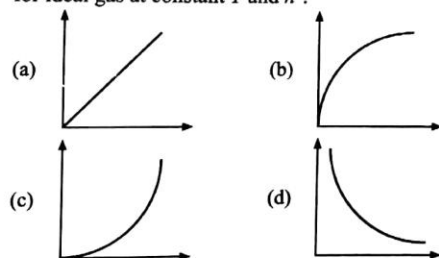
Pressure in atm



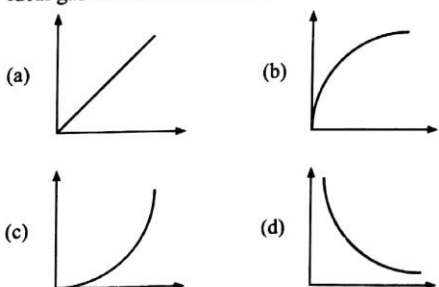
50. Which of the following graph is in accordance to the Maxwell distribution of molecular speeds and its dependence on temperature?



51. Which of the following graphs represents $\frac{1}{V^2}$ vs P curve for ideal gas at constant T and n ?



52. Which of the following graph represents V vs $\frac{1}{P^2}$ for ideal gas at constant T and n ?



53. The ratio of rates of diffusion of SO_2 and CH_4 placed in a container in the mass ratio of 8 : 1 at the same temperature is :

(a) 1 (b) 2
(c) 3 (d) 4

54. The inversion temperature T_i (K) of hydrogen is ... (Given van der Waals' constants a and b are $0.244 \text{ atm litre}^2 \text{ mol}^{-2}$ and $0.027 \text{ litre mol}^{-1}$ respectively) :

(a) 440 (b) 220
(c) 110 (d) 330

55. The compressibility of gas is less than unity at STP. Therefore : (IIT 2000)

(a) $V_m > 22.4 \text{ litre}$ (b) $V_m < 22.4 \text{ litre}$
(c) $V_m = 22.4 \text{ litre}$ (d) $V_m > 44.8 \text{ litre}$

56. The rms speed of hydrogen is $\sqrt{7}$ times the rms speed of nitrogen. If T is the temperature of the gas, then : (IIT 2000)

(a) $T(\text{H}_2) = T(\text{N}_2)$ (b) $T(\text{H}_2) > T(\text{N}_2)$
(c) $T(\text{H}_2) < T(\text{N}_2)$ (d) $T(\text{H}_2) = \sqrt{7} T(\text{N}_2)$

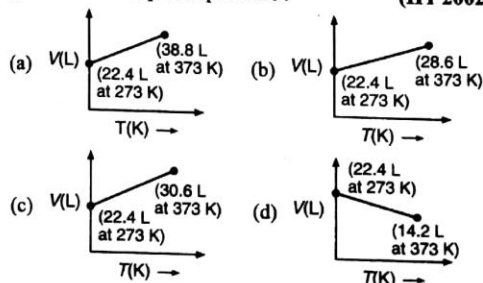
57. At 100°C and 1 atm, if the density of liquid water is 1.0 g cm^{-3} and that of water vapour is 0.0006 g cm^{-3} , then the volume occupied by water molecules in 1 litre of steam at that temperature is : (IIT 2000)

(a) 6 cm^3 (b) 60 cm^3
(c) 0.6 cm^3 (d) 0.06 cm^3

58. The root mean square speed of an ideal gas at constant pressure varies with density d as: (IIT 2001)

(a) d^2 (b) d
(c) $\sqrt{d}$ (d) $\frac{1}{\sqrt{d}}$

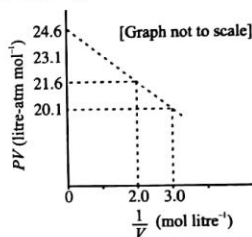
59. Which of the following volume (V) vs. temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure : (IIT 2002)



60. When the temperature is increased surface tension of water : (IIT 2002)

(a) increases
(b) decreases
(c) remains constant
(d) show irregular behaviour

61. Positive deviations from ideal gas behaviour takes place because of: (IIT 2003)
- (a) molecular interaction between atoms and $\frac{PV}{nRT} > 1$
 (b) molecular interaction between atoms and $\frac{PV}{nRT} < 1$
 (c) finite size of atoms and $\frac{PV}{nRT} > 1$
 (d) finite size of atoms and $\frac{PV}{nRT} < 1$
62. The root mean square speed of one mole of a monoatomic gas having molar mass M is u_{rms} . The relation between the average kinetic energy (E) of the gas and u_{rms} is: (IIT 2004)
- (a) $u_{\text{rms}} = \sqrt{\frac{3E}{2M}}$ (b) $u_{\text{rms}} = \sqrt{\frac{2E}{3M}}$
 (c) $u_{\text{rms}} = \sqrt{\frac{2E}{M}}$ (d) $u_{\text{rms}} = \sqrt{\frac{E}{3M}}$
63. The ratio of the rate of diffusion of helium and methane under identical conditions of pressure and temperature is: (IIT 2005)
- (a) 4 (b) 2
 (c) 1 (d) 0.5
64. A monoatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equal to unity. The molar heat capacity of gas is: (IIT 2006)
- (a) $2.0 R$ (b) $1.5 R$
 (c) $2.5 R$ (d) 0
65. The term that accounts for the attractive forces present in a real gas in the van der Waals' equation is: (IIT 2009)
- (a) nb (b) $\frac{n^2 a}{V^2}$
 (c) $-\frac{an^2}{V^2}$ (d) $-nb$
66. At 400 K, the root mean square (rms) speed of a gas X (molar mass 40) is equal to the most probable speed of a gas Y at 60 K. The molar mass of gas Y is: (IIT 2009)
- (a) 2 (b) 4
 (c) 6 (d) 8
67. For one mole of a van der Waals' gas when $b=0$ and $T=300$ K, the PV vs. $1/V$ plot is shown below. The value of the van der Waals' constant a (atm.litre²mol⁻²) is: (IIT 2012)



- (a) 1.0 (b) 4.5
 (c) 1.5 (d) 3.0
68. 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: [JEE (Main) 2013]
- (a) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$
 (b) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$
 (c) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$
 (d) $C^* : \bar{C} : C = 1.128 : 1.225 : 1$

SOLUTIONS (One Answer Correct)

1. (c) $\therefore P' = P_T \cdot X_M$
and $V' = V_T \cdot X_M$
where X_M is mole fraction
Also $\frac{P'}{P_T} = \text{Pressure fraction i.e., } X_P$
and $\frac{V'}{V_T} = \text{Volume fraction i.e., } X_V$
 $\therefore X_M = X_P = X_V$
2. (a) $PV = RT$ for ideal gases.
3. (d) Temperature is mass independent.
4. (d) $Z = \frac{P_C V_C}{RT_C}$; Also, gaseous molecules showing H-bonding show maximum deviations in Z due to increase in molecular attractions (e.g., Z for NH_3 , H_2O , $\text{CH}_3\text{OH} \approx 0.22$ to 0.24)
5. (d) Volume of molecules is negligible in comparison of total volume occupied by gas. About 99.9% volume of vessel is not occupied by gas molecules. The volume in which neither of the gas molecules is present $= \frac{99.9 \times 22.4}{100} = 22.3776$ litre.
6. (a) $Z = \frac{PV}{nRT} = 0.5$
Now, $\left[P + \frac{n^2 a}{V^2} \right] [V - nb] = nRT$
 $\left[P + \frac{n^2 a}{V^2} \right] [V] = nRT$ (b is negligible)
 $PV^2 - nRTV + n^2 a = 0$
 $\therefore V = \frac{nRT \pm \sqrt{n^2 R^2 T^2 - 4n^2 a \times P}}{2P}$
Since, V is constant at given P and T and thus, discriminant is $= 0$
 $\therefore n^2 R^2 T^2 = 4n^2 aP$
or $a = \frac{R^2 T^2}{4P} = \frac{(0.0821)^2 \times (273)^2}{4 \times 100}$
 $= 1.256 \text{ litre}^2 \text{ mol}^{-2} \text{ atm}$
7. (a) $\left[P + \frac{a}{V^2} \right] [V - b] = RT$
 $\therefore \left[P + \frac{a}{V^2} \right] V = RT$ (b is negligible)
or $V^2 P - RTV + a = 0$
 $V = \frac{+RT \pm \sqrt{R^2 T^2 - 4Pa}}{2P}$
Since, V is constant at given P and T , V can have only one value or discriminant $= 0$
 $\therefore R^2 T^2 = 4Pa$
or $a = \frac{R^2 T^2}{4P} = \frac{(0.0821)^2 \times (273)^2}{4 \times 34.98} = 3.59 \text{ dm}^6 \text{ atm mol}^{-2}$
8. (b) $PV = \frac{w}{M} RT$ (for vapours of H_2O)
 $P = 3.6 \times 10^3 \text{ Pa}$; $V = 2 \times 10^{-3} \text{ m}^3$;
 $T = 300 \text{ K}$
 $\therefore w_{\text{H}_2\text{O}} = \frac{3.6 \times 10^3 \times 18 \times 2 \times 10^{-3}}{8.314 \times 300}$
 $= 0.052 \text{ kg}$
or $w_{\text{H}_2\text{O}} = 52 \text{ g}$
Since, relative humidity $= 60\%$ therefore amount of $\text{H}_2\text{O} = 52 \times 0.6 = 31.2 \text{ g}$
9. (d) Molar ratio of N_2 and CO is $3:2$
 $\therefore$ Pressure ratio of N_2 and CO is $3:2$, i.e., 300 bar and 200 bar respectively
 $\frac{n_{\text{N}_2}}{n_{\text{CO}}} = \sqrt{\frac{M_{\text{CO}}}{M_{\text{N}_2}}} \times \frac{P_{\text{N}_2}}{P_{\text{CO}}} = \frac{300}{200} = \frac{3}{2}$
10. (b) $Z = \frac{PV}{nRT}$
 $\therefore n = \frac{PV}{ZRT} = \frac{1 \times 1}{1.2 \times 0.0821 \times 273} = 0.037$
 $\therefore$ Number of molecules $= 0.037 \times 6.023 \times 10^{23} = 2.23 \times 10^{22}$
11. (d) Ideal gas does not show cooling or heating.
12. (d) Due to H-bonding in NH_3 .
13. (b) Dry ice is solid CO_2
 $\therefore P \times 5 = \frac{0.44}{44} \times 0.0821 \times 300$
 $P = 0.049 \text{ atm}$
14. (b) $PV = \frac{w}{M} RT$
 $\therefore M = \frac{w}{V \cdot P} RT = \frac{1.33 \times 0.0821 \times 423 \times 760}{764} = 46$
molar mass of NO_2 is 46 g mol^{-1} .
15. (b) R.H. $= \frac{\text{Partial pressure of } \text{H}_2\text{O}_v}{\text{Saturated V.P. of } \text{H}_2\text{O}} \times 100$
16. (c) $PV = \frac{w}{M} RT$
 $\therefore PM = dRT$
or $d = \frac{PM}{RT}$
 $Pd = \frac{P^2 M}{RT}$
 $\therefore \frac{d[Pd]}{dP} = \frac{2PM}{RT} = 20$
 $\therefore T = \frac{2 \times 8.21 \times 30}{0.0821 \times 20} = 300 \text{ K}$
17. (a) $\left[P + \frac{a}{V^2} \right] [V - b] = RT$
 $\therefore PV + \frac{a}{V} = RT$
or $PV^2 + a - RTV = 0$

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

(A given P and T only one value of V exists, thus discriminant is zero)

18. (b) $PV = nRT$

$$n_{\text{Na}} = \frac{PV}{RT} = \frac{50 \times 2}{0.0821 \times 1273} = 0.9568,$$

$$\therefore \text{No. of atoms} = 0.9568 \times 6.023 \times 10^{23} = 5.76 \times 10^{23}$$

19. (b) $n = \frac{PV}{RT} = \frac{PV}{kN \cdot T} \left(\frac{R}{N} = k \right)$

$$\therefore n \times N = \frac{PV}{kT} = \text{No. of molecules}$$

20. (b) Let a g of Ne and b g of Ne and Ar be present respectively

$$a + b = 30 \quad \dots(1)$$

$$\text{K.E. of mixture} = \frac{3}{2} \left[\frac{a}{20} + \frac{b}{40} \right] RT = 3 \times 10^3$$

$$\frac{a}{20} + \frac{b}{40} = \frac{3 \times 10^3 \times 2}{3 \times 8.314 \times 250} = 0.96$$

$$\therefore 2a + b = 38.48 \quad \dots(2)$$

$$\therefore a = 8.48 \text{ and } b = 21.52$$

$$\therefore \% b \text{ (i.e., Ar)} = \frac{21.52}{30} \times 100 = 71.7\%$$

21. (a) $\therefore u_{\text{rms}} = \sqrt{\frac{3P}{d}}$

$$\therefore \Delta u = \sqrt{\frac{3}{d}} \times (\sqrt{P_2} - \sqrt{P_1})$$

$$= \sqrt{\frac{3}{0.75}} \times [\sqrt{9 \times 10^4} - \sqrt{4 \times 10^4}]$$

$$= \sqrt{\frac{3}{0.75}} \times 100 = 200 \text{ msec}^{-1}$$

22. (a) Monoatomic gas: $\gamma = \frac{5}{3}$; $C_v = \frac{3}{2}R$ and $C_p = \frac{5}{2}R$

Diatomic gas: $\gamma = \frac{7}{5}$; $C_v = \frac{5}{2}R$ and $C_p = \frac{7}{2}R$

For mixture of 1 mole each: $C_v = \frac{\left(\frac{3}{2} + \frac{5}{2}\right)R}{2}$ and

$$C_p = \frac{\left(\frac{5}{2} + \frac{7}{2}\right)R}{2}$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{6R}{4R} = \frac{3}{2} = 1.5$$

23. (b) $P = \frac{d}{M} RT$

$$\therefore \frac{d}{P} \propto \frac{1}{T}$$

or $\frac{d_1}{p_1} \times \frac{p_2}{d_2} = \frac{1}{283} \times \frac{383}{1}$

$$\therefore \frac{d_2}{p_2} = \frac{d_1}{p_1} \times \frac{283}{383}$$

$$\therefore \frac{d_2}{P_2} = \frac{283 \cdot X}{383} = \frac{283X}{383}$$

24. (c) 0.1 mole has 0.3 N atom of gas.

25. (a) $P'_{O_2} = P_M \times \text{mole fraction of } O_2$

$$\therefore \frac{P'}{P_M} = \text{mole fraction } O_2 = \frac{\frac{w}{32}}{\frac{w}{16} + \frac{w}{32}} = \frac{1}{3}$$

26. (b) It is definition of Boyle's temperature.

27. (b) $U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$; $U_{\text{av}} = \sqrt{\frac{8RT}{\pi M}}$

$$\therefore \frac{u_{\text{rms}}}{u_{\text{av}}} = \sqrt{\frac{3\pi}{8}} = 1.086$$

28. (b) Av. K.E. = $\frac{3}{2} \frac{RT}{N} = \frac{3}{2} kT$

29. (b) $\frac{P'_{H_2}}{P_M} = \text{mole fraction } H_2 = \frac{\frac{w}{2}}{\frac{w}{2} + \frac{w}{16}} = \frac{8}{9}$

30. (c) Greater the value of ' a ' i.e., intermolecular forces of attraction for a gas, the more easily the gas will be liquefied.

31. (c) At a given temperature (see equilibrium exist) kinetic energy of gas liquid = $\frac{3}{2} RT$

32. (d) Graham's law of diffusion; $r \propto \sqrt{\frac{1}{M}}$

33. (a) $u_{\text{AV}} = \sqrt{\frac{8RT}{\pi M}}$; $\frac{u_1}{u_2} = \sqrt{\frac{T_1}{T_2}}$

$$\therefore \frac{0.3}{u_2} = \sqrt{\frac{300}{1200}} \text{ or, } u_2 = \sqrt{\frac{1200}{300}} \times 0.3 = 0.6 \text{ ms}^{-1}$$

34. (c) Pressure correction in gas equation by van der Waals' is $\frac{a}{V^2}$ for 1 mole. Thus $P_{\text{gas}} = \left[P + \frac{a}{V^2} \right]$

35. (b) HCl diffuses at a slower rate because of its higher molar mass.

36. (b) Density of a gas, $e = \frac{PM}{RT}$; $e \propto P$ and $e \propto \frac{1}{T}$

37. (a) $\frac{r_{\text{CH}_4}}{r_x} = \sqrt{\frac{M_x}{M_{\text{CH}_4}}}$

$$\text{Thus, } \frac{2}{1} = \sqrt{\frac{M_x}{16}} \therefore M_x = 4 \times 16 = 64.$$

38. (d) K.E. = $\frac{3}{2} \frac{RT}{N}$

39. (a) $PV = \frac{1}{3} mnu^2$

$$\text{for one mole, } PV = \frac{1}{3} Mu^2 \therefore P \propto u^2$$

40. (d) $\frac{P'_{H_2}}{P_M} = \text{mole fraction of } H_2 = \frac{\frac{w}{2}}{\frac{w}{2} + \frac{w}{30}} = \frac{15}{16}$

41. (c) Due to higher molar mass of $C_6H_5 \cdot CH_3$.

42. (a) Due to higher repulsive forces.

43. (c) $U_{\text{rms}} = \frac{3RT}{M}$

Thus, $(U_{\text{rms}})_{\text{H}_2} = \sqrt{\frac{3 \times R \times 50}{2}}$ at 50 K ... (1)

$(U_{\text{rms}})_{\text{O}_2} = \sqrt{\frac{3 \times R \times 800}{32}}$ at 800 K ... (2)

So, $\frac{(U_{\text{rms}})_{\text{H}_2}}{(U_{\text{rms}})_{\text{O}_2}} = \sqrt{\frac{50 \times 32}{2 \times 800}} = 1$

44. (b) Use $\eta_0 = \frac{\nu}{t} \propto \sqrt{\frac{1}{M}}$ (P, T)

$\frac{\eta_{\text{H}_2}}{\eta_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{H}_2}}}$, $\frac{\eta_{\text{H}_2}}{\eta_{\text{O}_2}} = \frac{x}{5} \times \frac{t}{x} = \sqrt{\frac{32}{2}}$ $\therefore t = 20 \text{ sec}$

45. (b) $\frac{PV}{nRT} = Z$ (compressibility factor) for an ideal gas $Z = 1$.

46. (d) Dipole moment gives rise to higher value of a for H_2O in spite of low molar mass

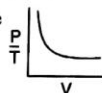
47. (c) According to Graham's law of diffusion $r \propto P\sqrt{\frac{1}{M}}$ at constant temperature.

$\therefore \frac{r_A}{r_B} = \frac{P_A}{P_B} \sqrt{\frac{M_B}{M_A}} = \frac{P_A}{P_B} \times \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}}$

48. (c) A gas will approach ideal behaviour at high temperature and low pressure.

49. (d) Fig. (a) represents Charles' law; Fig. (b) represents Boyle's law; Fig. (c) represents P - T law; Fig. (d) do not obey ideal gas laws as $PV = nRT$ or $\frac{P}{T} = \frac{K}{V}$. An

increase in V will show decrease in $\frac{P}{T}$ like



P - V curve in Boyle's law.

50. (c) Follow text.

51. (c) Let $Y = \frac{1}{V^2}$ and $X = P = \frac{K}{V}$

$\therefore V = \frac{1}{\sqrt{Y}}$

Also $X = K\sqrt{Y}$

$\therefore Y = K^2 \cdot X^2$

i.e. curve (c).

52. (b) Let $\frac{1}{P^2} = Y$

$\therefore P = \frac{1}{\sqrt{Y}}$

if $X = V = \frac{K}{P} = K\sqrt{Y}$

or $X^2 = K^2 Y$ i.e. curve (b).

53. (a) $\frac{r_{\text{SO}_2}}{r_{\text{CH}_4}} = \sqrt{\frac{16}{64} \times \frac{8}{64} \times \frac{16}{1}} = 1$

54. (b) $T_i = \frac{2a}{Rb} = \frac{2 \times 0.244}{0.027 \times 0.0821} = 220.14$

55. (b) $Z < 1$ or $\frac{PV}{nRT} < 1$

Thus, $V_m < 22.4 \text{ litre}$

56. (c) $u_{\text{rms H}_2} = \sqrt{\frac{3RT_1}{2}}$ and $u_{\text{rms N}_2} = \sqrt{\frac{3RT_2}{28}}$

$u_{\text{rms H}_2} = \sqrt{7} \times u_{\text{rms N}_2}$

$u_{\text{rms H}_2} = \sqrt{7} \times u_{\text{rms N}_2}$

or $\sqrt{\frac{3RT_1}{2}} = \sqrt{7} \times \sqrt{\frac{3RT_2}{28}}$

$\therefore \frac{T_1}{2} = \frac{T_2}{4}$ or $T_2 = 2T_1$ or $T_{\text{N}_2} > T_{\text{H}_2}$

57. (c) Mass of 1000 mL steam = $1000 \times 0.0006 = 0.6 \text{ g}$

$\therefore$ Volume of liquid water = $\frac{0.6}{1} = 0.6 \text{ cm}^3$

58. (d) $u_{\text{rms}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$

59. (c) Use $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

60. (b) Forces of attractions are weakened as the temperature increases.

61. (c) For positive deviations $Z > 1$, i.e., the condition when repulsive forces predominates. Also, at high P , V is small and b cannot be ignored, but the factor $\frac{a}{V^2}$ can be

neglected in comparison to P . Thus, $Z = 1 + \frac{Pb}{RT}$

62. (c) $u_{\text{rms}} = \sqrt{\frac{3RT}{M}}$ and $\text{KE} = \frac{3}{2} RT$

$\therefore u_{\text{rms}} = \sqrt{\frac{2E}{M}}$

63. (b) $\frac{\eta_{\text{He}}}{\eta_{\text{CH}_4}} = \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \sqrt{\frac{16}{4}} = 2$

64. (a) Let P, V be the pressure and volume of gas at temperature T .

$P_1 V_1 = RT$

$P_2 (V_1 + dV) = R(T + 1)$

$\therefore P_2^2 = RT + R$ $\left(\because \frac{P_2 V_2}{V_1 + dV} = 1 \right)$

$\therefore 2 \left(\frac{\partial P_2}{\partial T} \right)_V = R$

$\therefore \left(\frac{\partial P_2}{\partial T} \right) = \frac{R}{2}$

$\therefore C = C_v + \frac{\partial P}{\partial T} = \frac{3R}{2} + \frac{R}{2} = 2R$

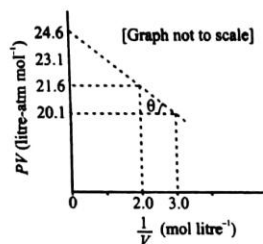
65. (b) van der Waals' equation has pressure correction term $\left[p + \frac{n^2 a}{V^2} \right]$ due to attraction forces.

66. (b) $u_{\text{rms X}} = \sqrt{\frac{3R \times 400}{40}}$

$u_{\text{MPY}} = \sqrt{\frac{2R \times 60}{M}}$

$\therefore M = 4$

67. (c)



van der Waals' equation for 1 mol of real gas is

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

Given that $b = 0$

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

$$\therefore PV = RT - \frac{a}{V}$$

... (i)

Following $y = mx + c$ for the curve PV vs $1/V$ Slope = $-a$

$$\text{Slope} = \frac{21.6 - 20.1}{2 - 3} = -1.5$$

$$\therefore a = 1.5$$

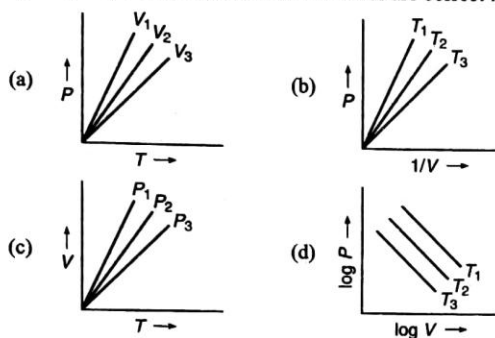
$$68. (b) u_{m.p.} : u_{A.V.} : u_{rms} :: \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}}$$

$$:: 1 : 1.128 : 1.225$$

$$\text{Thus } C^* : \bar{C} : C :: 1 : 1.225 : 1.128$$

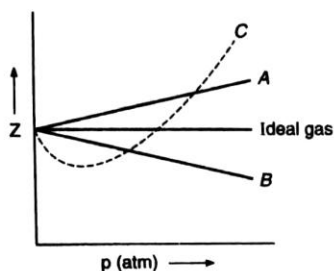
OBJECTIVE PROBLEMS (More Than One Answer Correct)

1. For 1 mole of an ideal gas $V_1 > V_2 > V_3$ in Fig. (a), $T_1 > T_2 > T_3$ in Fig. (b), $P_1 > P_2 > P_3$ in Fig. (c) and $T_1 > T_2 > T_3$ in Fig. (d), then which curves are correct :



2. A mixture of SO_2 and O_2 in the molar ratio 16:1 is diffused through a pin hole for successive effusions three times to give a molar ratio 1:1 of diffused mixture. Which one are correct if diffusion is made at same P and T in each operation?
- Eight operations are needed to get 1:1 molar ratio
 - Rate of diffusion for $\text{SO}_2 : \text{O}_2$ after 8 operations is 0.707
 - Six operations are needed to get 2:1 molar ratio for SO_2 and O_2 in diffusion mixture
 - Rate of diffusion for SO_2 and O_2 after 6 operations is 2.41
3. A graph plotted between $\log V$ and $\log T$ for 2 mole of gas at constant pressure of 0.0821 atm. V and T are in litre and K respectively. Which of the following statements are correct?
- The curve is straight line with slope -1
 - The curve is straight line with slope $+1$
 - The intercept on Y -axis is equal to 2
 - The intercept on Y -axis is equal to 0.3010
4. A gas obeys $P(V - b) = RT$. Which of the following are correct about this gas?
- Isochoric curves have slope $= \frac{R}{V - b}$
 - Isobaric curves have slope $\frac{R}{P}$ and intercept b
 - For the gas compressibility factor $= 1 + \frac{Pb}{RT}$
 - The attraction forces are overcome by repulsive forces
5. Which are correct for an ideal gas :
- $\left(\frac{\partial P}{\partial V_M}\right)_{T_c} = 0$
 - $\left(\frac{\partial E}{\partial V}\right)_T = 0$
 - $\left(\frac{\partial E}{\partial P}\right)_T \neq 0$
 - $\left(\frac{\partial n}{\partial V}\right)_{P, T} \neq 0$
6. Which are correct for an ideal gas :
- $\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = 0$
 - $\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \cdot \left(\frac{\partial T}{\partial P}\right)_V = -1$
 - $\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial V}\right)_P \cdot \left(\frac{\partial V}{\partial P}\right)_T = -1$
 - Thermal expansion coefficient of gas $= \frac{P}{T}$
Isothermal compressibility constant $= \frac{P}{T}$
7. Select the correct statements :
- A gas cannot be compressed below its critical temperature
 - Critical temperature is the highest temperature at which liquid and gaseous phase can coexist
 - The fraction of molecules having their most probable speed increases with rise in temperature
 - Ideal gas can be liquified at high pressure
8. Select the incorrect statements :
- Compressibility factor for 1 mole of gas at critical conditions is $8/3$
 - All molecules of gas move with same speed
 - The diameter of gaseous molecules are much smaller than the average distance travelled between collision
 - Saturated vapours do not obey gas laws except Dalton's law
9. Select the correct statements :
- Greater is humidity, lesser will be rate of evaporation of water
 - Greater is the humidity, lesser will be density of air
 - If room temperature = dew point; relative humidity = 100%
 - Dew point is the temperature at which the gas at given atmospheric condition becomes saturated with $\text{H}_2\text{O}(v)$
10. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules :
- are above the inversion temperature
 - exert no attractive forces on each other
 - do work equal to loss in kinetic energy
 - collide without loss of energy

11. If 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 increases
12. The given graph represents the variation of Z (compressibility factor) vs. P for three real gases A, B and C. Identify the correct statement : (IIT 2006)



- (a) For the gas A, $a=0$ and its dependence on P is linear at all pressure
 (b) For the gas B, $b=0$ and its dependence on P is linear at all pressure
 (c) For the gas C, which is typical real gas for which $a \neq 0$, $b \neq 0$. By knowing the minima and the point of intersection with $Z=1$, a and b can be calculated
 (d) At high pressure, the slope is positive for all real gases
13. A gas described by van der Waals' equation : (IIT 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 pressure
 (c) is characterised by van der Waals' coefficients that are dependent on the identity of gas but are independent of the temperature
 (d) has the pressure that is lower than the pressure exerted by the same gas behaves ideally
14. According to kinetic theory of gases : (IIT 2011)
 (a) Collisions are always elastic
 (b) Heavier molecules transfer more momentum to the wall 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
15. Which of the following are correct statements :
 (a) Higher is $\frac{T_C}{P_C}$, larger is excluded volume
 (b) Higher is V_C , larger is excluded volume
 (c) Higher is $\frac{T_C}{V_C}$, more is van der Waals' constant for attraction
 (d) Smaller is size of molecule, lesser will be excluded volume
16. Select the correct statements for ideal gas :
 (a) Joule Thomson coefficient for ideal gas is zero
 (b) Ideal gas does not have intermolecular attractions among their molecules
 (c) Ideal gas can never be liquefied
 (d) Gaseous phase can not exist at zero kelvin
17. Select the correct statement :
 (a) Temperature does not change during phase transition equilibria
 (b) Kinetic energy of liquid molecules is directly proportional to temperature
 (c) Liquid phase does not exist above critical temperature
 (d) The density of gas and liquid phase is equal at critical condition
18. Select the correct statements :
 (a) Random molecular motion by gaseous molecules is confirmed by diffusion
 (b) The boiling point of liquid N_2 is -196°C
 (c) He is the only noble gas which does not behave ideally at any condition.
 (d) Pressure of gas calculated by using van der Waals' equation is smaller than the pressure calculated by using ideal gas equation.

SOLUTIONS (More Than One Answer Correct)

1. (b,d) $PV = RT$ if $P_1 > P_2, V_1 < V_2$.

Also, $\log P = -\log V + \log RT$

2. (a,b,c) $(f_1)^X = \frac{n'_{SO_2}}{n_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}}$, where, n_{SO_2} and n_{O_2} are mole present initially.

$$\text{or } X \log f_1 = \log \left[\frac{n'_{SO_2}}{n_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}} \right]$$

$$\therefore X \log \sqrt{\frac{M_{O_2}}{M_{SO_2}}} = \log \left[\frac{n'_{SO_2}}{n_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}} \right]$$

$$X \log \sqrt{\frac{32}{64}} = \log \frac{1}{1} \times \frac{1}{16} \therefore X = 8;$$

$$\text{Also } \frac{n_1}{n_2} = \frac{\eta_1}{\eta_2} = \sqrt{\frac{32}{64}} = 0.707$$

If $X = 6$ then

$$6 \log \sqrt{\frac{32}{64}} = \log \left[\frac{n'_{SO_2}}{n_{O_2}} \times \frac{n_{O_2}}{n_{SO_2}} \right]$$

$$= \log \left[\frac{n'_{SO_2}}{n_{O_2}} \times \frac{1}{16} \right]$$

$$\frac{n'_{SO_2}}{n_{O_2}} = 2:1$$

Rate of diffusion is $\frac{\eta_1}{\eta_2} = \sqrt{\frac{M_2}{M_1}}$, i.e., 0.707 in each operation.

3. (b,d) $PV = nRT$ or $\log V = \log T + \log \frac{nR}{P}$

$$\text{Slope} = \tan \theta = \tan 45^\circ = 1$$

Intercept

$$= \log \frac{nR}{P} = \log \left[\frac{2 \times 0.0821}{0.0821} \right] = 0.3010$$

4. (a,b,c,d) $P(V-b) = RT$

$$\therefore P = \frac{R}{(V-b)} \cdot T \quad \text{slope} = \frac{R}{V-b}$$

$$PV - Pb = RT$$

$$V = \frac{RT}{P} + b$$

$$\text{slope} = \frac{R}{P} \text{ and intercept } b$$

$$Z = \frac{PV}{RT} = 1 + \frac{Pb}{RT};$$

$Z > 1$, i.e., repulsive forces predominates.

5. (a,b,d) $\left(\frac{\partial E}{\partial P} \right)_T = \text{zero}$

6. (b,c,d) Thermal expansion coefficient $\alpha = \frac{\left(\frac{\partial V}{\partial T} \right)_P}{V} = \frac{1}{T}$
(Use $PV = RT$)

$$\text{Isothermal compressibility constant} = - \frac{\left(\frac{\partial V}{\partial P} \right)_T}{V} = \frac{1}{P}$$

7. (b,c) Ideal gas have no forces of attractions.

8. (a,b) $Z = \frac{P_C V_C}{RT_C} = \frac{3}{8}$; each molecule move with altogether different speed.

9. (a,b,c,d) All are facts.

10. (b,d) No work is required to tear apart molecules due to the absence of attractive forces in an ideal gas. Also collision are perfectly elastic.

11. (a,b) When a gas is expanded at constant temperature, then the kinetic energy of the molecules remain the same, but the pressure decreases because $V \propto \frac{1}{P}$

12. (a,c,d) Follow Concepts of Physical Chemistry by Dr. P. Bahadur, G.R. Bathla Publications, Meerut.

13. (a,c,d) $\left[P + \frac{a}{V^2} \right] = [V - b] = RT$

$$\text{If } V \text{ is large } PV = RT \quad \left(\frac{a}{V^2} \text{ and } b \text{ are negligible} \right)$$

14. (a,b,c,d) All are assumptions of kinetic theory of gases and Maxwell probable distribution of molecular speeds.

15. (a,b,c,d) $T_C = \frac{8a}{27b^2}$; $V_C = 3b$; $P_C = \frac{a}{27b^2}$ and excluded volume, $b = 4 \times N \times v$

16. (a,b,c,d) All are facts.

17. (a,b,c,d) —do—

18. (a,b,c,d) —do—

COMPREHENSION BASED PROBLEMS

Comprehension 1 : Gases show ideal gas behaviour in Boyle temperature range. Assume for the air this temperature range between 300 K to 900 K.

An open vessel at 27°C is heated until 3/5th of the air in it has been expelled. Assuming that the volume of the vessel remains constant,

- [1] The temperature at which vessel was heated.
 - (a) 750 K
 - (b) 600 K
 - (c) 500 K
 - (d) 400 K
- [2] The air escaped out if vessel is heated to 900 K.
 - (a) n
 - (b) $\frac{n}{3}$
 - (c) $\frac{2n}{3}$
 - (d) $\frac{n}{2}$
- [3] The temperature at which half of the air escapes out.
 - (a) 750 K
 - (b) 600 K
 - (c) 500 K
 - (d) 400 K

Comprehension 2 : Gaseous pressure is measured by barometer. The barometric tube must be exactly vertical, otherwise the pressure reading will not be accurate.

A 10 cm column of air is trapped by a column of Hg of 8 cm long. The capillary tube is horizontally fixed at 1 atm pressure. Calculate the length of air column when the tube is fixed at same temperature :

- [1] The pressure of air measured when tube is held vertically with open end up is :
 - (a) 11.61 cm
 - (b) 9.05 cm
 - (c) 11.18 cm
 - (d) 10.18 cm
- [2] The pressure of air (in cm) when tube is held vertically with open end down.
 - (a) 11.61
 - (b) 9.6
 - (c) 11.18
 - (d) 10.3
- [3] The pressure of air (in cm) when tube is held at 45° from horizontal with open end up.
 - (a) 9.3
 - (b) 10.3
 - (c) 11.3
 - (d) 11.61

Comprehension 3 : An open glass bulb containing air was heated from 27°C to 227°C. Assuming ideal nature.

- [1] If 200 mL of air measured at 227°C was expelled during heating, the volume of bulb in mL must be :
 - (a) 500
 - (b) 400
 - (c) 300
 - (d) 200
- [2] If 200 mL of air measured at 27°C was expelled during heating, the volume of bulb in mL must be:
 - (a) 200
 - (b) 300
 - (c) 400
 - (d) 500

Comprehension 4 : Ideal gas equation is represented as $PV = nRT$. Gases present in universe were found ideal in the Boyle's temperature range only and deviated more from ideal gas behaviour at high pressure and low temperature. The

deviations are explained in terms of compressibility factor Z . For ideal behaviour $Z = \frac{PV}{nRT} = 1$. The main cause to show

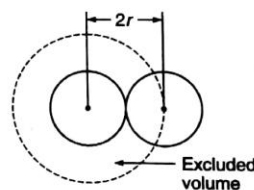
deviations were due to wrong assumptions made about forces of attractions (which becomes significant at high pressure) and volume occupied by molecules V in $PV = nRT$ is supposed to be volume of gas or, the volume of container in which gas is placed by assuming that gaseous molecules do not have appreciable volume. Actually volume of the gas is that volume in which each molecule of a gas can move freely. If volume occupied by gaseous molecule is not negligible, then the term V should be replaced by the ideal volume which is available for free motion of each molecules of gas in 1 mole gas

$$V_{\text{actual}} = \text{volume of container} - \text{volume occupied by molecules} \\ = V - b$$

where b represents the effective volume of co-volume or excluded volume occupied by molecules present in one mole of gas.

Similarly for n mole gas $V_{\text{actual}} = V - nb$. The excluded volume can be calculated by considering bimolecular collisions. The excluded volume is the volume occupied by the sphere of $2r$ for each pair of molecule.

Thus, excluded volume for one pair of molecules



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

$\therefore$ excluded volume for 1 molecule

$$= \frac{2}{3} \times 8 \pi r^3 \quad \dots(ii)$$

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

$$= 4 \times \text{volume of one molecule} = 4v$$

$\therefore$ excluded volume for N molecules

$$= 4Nv = b$$

$$(b = 4Nv, \text{ where } N \text{ is Avogadro's No.})$$

[1] Which of the following statements are correct?

- I. Larger is the value of $\frac{T_c}{P_c}$ for a gas larger would be its excluded volume.
- II. Larger is the excluded volume of gas, more will be its critical volume.

- III. The slope for an isochore obtained for a gas showing $P(V-b) = RT$ is $\left[\frac{R}{V-b}\right]$.
- IV. The excluded volume for He is more than H_2 .
 (a) I, II, III (b) I, II, IV
 (c) II, III, IV (d) III, IV
- [2] As the pressure approaching zero i.e., at very low pressure, the curves plotted between compressibility factor Z and P for n mole of gases have the following characteristics:
 I. The intercept on y-axis leads to a value of unity
 II. The intercept on y-axis leads to a value of 'n'
 III. The curves possess same slope for different gases at same temperature
 IV. The curves possess different slopes for different gases at same temperature
 V. The curves possess same slope for a gas at different temperatures
 (a) I, IV, V (b) II, III
 (c) II, III, IV (d) II, III, V
- [3] Assuming the molecules of gas as hard sphere of radius 2.0×10^{-10} m the fraction of volume occupied by the molecules to the total volume of a given mass of gas at 27°C and at 1 bar pressure and 10 bar pressure respectively are:
 (a) 99.9%, 99% (b) 0.082%, 0.82%
 (c) 99%, 90% (d) 1%, 10%
- [4] The compressibility factor for N_2 at -50°C and 800 atm pressure is 1.95. The mole of N_2 required to fill up a balloon of 100 L capacity are:
 (a) 2.24×10^3 L (b) 2.24×10^2 L
 (c) 2.24 L (d) 22.4 L
- [5] Which of the following statements are correct?
 I. Rise in compressibility factor Z with increase in pressure is due to 'a'
 II. Rise in compressibility factor Z with increase in pressure is due to 'b'
 III. Ideal gas do not exist but is a useful concept
 IV. For 1 mole of a van der Waals' gas,

$$Z = 1 + \frac{bP}{RT} - \frac{a}{RTV} + \frac{ab}{RTV^2}$$

 (a) I, II, III, IV (b) II, III, IV
 (c) I, III, IV (d) I, IV
- [6] The ratio of coefficient of thermal expansion $\alpha = \frac{\left(\frac{\partial V}{\partial T}\right)_P}{V}$ and the isothermal compressibility $K = \frac{\left(\frac{\partial V}{\partial P}\right)_T}{V}$ for an ideal gas is:
 (a) $-\frac{P}{T}$ (b) $\frac{P}{T}$
 (c) $\frac{T}{P}$ (d) $-\frac{T}{P}$

SOLUTIONS

Comprehension 1

- [1] (a) Let initial mole of gas at 27°C are n .
 On heating $3/5$ mole of air are escaped out at temperature, T .
 Thus, mole of air left at temperature, $T = n - \frac{3}{5}n = \frac{2n}{5}$
 Now, under similar conditions of P and V

$$n_1 T_1 = n_2 T_2$$

$$n \times 300 = \frac{2n}{5} \times T$$

$$\therefore T = 750 \text{ K}$$

 [2] (c) At $T_1 = 300 \text{ K}$, No. of mole = n , $T_2 = 900 \text{ K}$,
 No. of mole = n_1

$$\therefore 300 \times n = 900 \times n_1 \quad \therefore n_1 = \frac{1}{3}n$$

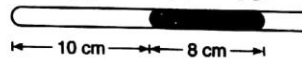
$$\therefore \text{No. of mole escaped out} = n - \frac{1}{3}n = \frac{2}{3}n \text{ mol}$$

 [3] (b) When half of the air escaped out at temp. T , then $n = \frac{n}{2}$

$$\therefore n \times 300 = \frac{n}{2} \times T$$

$$\therefore T = 600 \text{ K} = 327^\circ\text{C}$$

Comprehension 2

- [1] (b) $P_1 V_1 = P_2 V_2$ or $P_1 l_1 a = P_2 l_2 a$


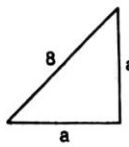
$$\therefore P_2 = 76 + 8 = 84 \text{ cm}$$

$$\therefore l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{84} = 9.05 \text{ cm}$$

 [2] (c) $P_1 l_1 a = P_2 l_2 a$

$$\therefore P_2 = 76 - 8 = 68 \text{ cm}$$

$$\therefore l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{68} = 11.18 \text{ cm}$$

 [3] (a) When the tube is held at 45° with open end up, the mass of Hg is borne partially by the gas and partially by the Hg. Vertical height of Hg is a measure of additional pressure on gas, i.e.,


$$l = \frac{8}{\sqrt{2}}$$

 Also $P_2 l_2 a = P_1 l_1 a$

$$\therefore l_2 = \frac{P_1 l_1}{P_2} = \frac{76 \times 10}{76 + \frac{8}{\sqrt{2}}} = 9.3 \text{ cm}$$

Comprehension 3[1] (c) Let volume of bulb be V mL $\therefore$ Volume of air at 300 K = V mLAfter heating volume of air at 500 K = $V + 200$ mL

$$\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{at constant } P)$$

$$\frac{V}{300} = \frac{V + 200}{500}$$

$$\therefore V = 300 \text{ mL}$$

[2] (d) Let volume of bulb be V mL

Volume of air at 300 K given out = 200 mL

$$\text{or} \quad \frac{200}{300} = \frac{V_2}{500}$$

$$\therefore V_2 = \frac{100000}{300}$$

$$\therefore \text{Volume of air at 500 K} = V + \frac{100000}{300}$$

$$\text{Therefore, } \frac{V}{300} = \frac{V + \frac{100000}{300}}{500}; \therefore V = 500 \text{ mL}$$

Comprehension 4

$$[1] (a) V_c = 3b, T_c = \frac{8a}{27Rb}, P_c = \frac{a}{27b^2}$$

Also, b for He = 0.1142 litre mol⁻¹ and b for H₂ is 0.1460 litre mol⁻¹

$$[2] (a) \frac{PV}{nRT} = Z$$

At very low P or $P \rightarrow 0$, $z = 1$ since ideal gases. Also, as the temperature increases Z approaches unity.[3] (b) At $P = 1$ bar

$$\text{Volume of gas} = \frac{nRT}{P} = \frac{n \times 0.0821 \times 300}{1} = 24.63 \times n \text{ L}$$

At $P = 10$ bar

$$\text{Volume of gas} = \frac{n \times 0.0821 \times 300}{10} = 2.463 \times n \text{ L}$$

Also, volume of molecules

$$= n \times \text{Avogadro's No.} \times \frac{4}{3} \pi r^3$$

$$= n \times 6.023 \times 10^{23} \times \frac{4}{3} \times 3.14 \times (2.0 \times 10^{-8})^3$$

$$= 20.17 \times n \text{ cm}^3$$

$$= 0.0202 \times n \text{ L}$$

At $P = 1$ bar

$$\therefore \frac{V_m}{V_g} = \frac{0.0202 \times n}{24.63 \times n} = 8.2 \times 10^{-4}$$

$$\text{or } 8.2 \times 10^{-2} \% = 0.082 \%$$

At $P = 10$ bar

$$\therefore \frac{V_m}{V_g} = \frac{0.0202}{2.463 \times n} = 8.2 \times 10^{-3}$$

$$\text{or } 8.2 \times 10^{-1} \% = 0.82 \%$$

$$[4] (a) Z = \frac{PV}{nRT}$$

$$\therefore n = \frac{800 \times 100}{1.95 \times 0.0821 \times 223} = 2.24 \times 10^3$$

[5] (b) There are facts.

$$[6] (b) PV = RT$$

$$\therefore P \partial V = R \cdot \partial T$$

$$\text{or } \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} = \frac{R \cdot V}{RT}$$

$$\text{or } \alpha = \frac{\left(\frac{\partial V}{\partial T} \right)_P}{V} = \frac{1}{T}$$

$$\text{Also, } P \cdot \partial V + V \cdot \partial P = 0$$

$$\therefore \left(\frac{\partial V}{\partial P} \right)_T = -\frac{V}{P}$$

$$\text{or } K = -\frac{\left(\frac{\partial V}{\partial P} \right)_T}{V} = \frac{1}{P}$$

STATEMENT EXPLANATION PROBLEMS

Read the following statements (S) and explanations (E). Choose the correct answers from the codes (a), (b), (c) and (d):

- (a) S is correct but E is wrong.
 (b) S is wrong but E is correct.
 (c) Both S and E are correct and E is correct explanation of S.
 (d) Both S and E are correct but E is not correct explanation of S.
- S : The product of pressure and volume of a fixed mass of gas is independent of temperature.
 E : The product of P and V depends upon temperature.
 - S : The increase in compressibility factor with increasing pressure is due to a .
 E : $Z = 1 + \frac{bP}{RT}$ for real gases can be obtained by neglecting $\frac{a}{V^2}$ term in van der Waals' equation.
 - S : A gas can be liquefied at $T = T_c$ and $P < P_c$.
 E : A gas can be liquefied when $T < T_c$ and $P < P_c$.
 - S : The gas is heated, if its temperature is less than its inversion temperature in Joule-Thomson effect.
 E : Heating effect in gas is noticed during Joule-Thomson effect when $T > T_i$.
 - S : It is not possible to liquefy an ideal gas.
 E : There exist no forces of attraction among the molecule of ideal gas.
 - S : All molecules in a gas are moving with same speed.
 E : Speed of molecules in a gas follows Maxwell's distribution law.
 - S : Average speed of molecules, if a gas in a container moving only in one dimension, will be zero.
 E : The molecules of gas are not collected in one direction.
 - S : The fraction of molecules having speed in the range u and $(u + du)$ of a gas of molar mass M at temperature T is the same as that of gas of molar mass of $2M$ and temperature $T/2$.
 E : The fraction of molecules having their speed within the range u to $(u + du) \propto \frac{M}{T}$.
 - S : Energy can be transferred between gaseous molecules during collisions but u_{rms} remains constant.
 E : The average kinetic energy of gaseous molecules remains constant as long as temperature is constant and therefore, u_{rms} remains unchanged during collision.
 - S : The compressibility factor for H_2 and He is $\left[1 + \frac{Pb}{RT}\right]$.
 E : The compressibility factor for H_2 and He can be derived from van der Waals' equation.
 - S : The numerical values of P_c, V_c, T_c are $\frac{a}{27b^2}, 3b$ and $\frac{8a}{27Rb}$ respectively.
 E : The compressibility factor Z at critical conditions is $\frac{3}{8}$.
 - S : The numerical value of a for H_2O is higher than C_6H_6 .
 E : H_2O shows H-bonding.
 - S : At low pressure van der Waals' equation is reduced to $\left[P + \frac{a}{V^2}\right]V = RT$.
 E : The compressibility factor corresponding to low pressure is given by $1 - \frac{RTV}{a}$.
 - S : Molar specific heat at constant volume of an ideal diatomic gas is $\left[\frac{3}{2}R + R\right]$.
 E : On heating one mole of an ideal diatomic gas at constant pressure for $1^\circ C$ rise in temperature, the increase in internal energy of gas is $\frac{7}{2}R$.
 - S : A vacuum is a space from which almost all gas has been removed.
 E : A vacuum is produced by pumping out all the air and other gases.
 - S : Gaseous molecules are assumed to be "point masses" occupying no volume.
 E : Gaseous molecules suffer no energy loss due to friction.
 - S : Compressibility factor Z according to van der Waals' equation may be written as $Z = \frac{1}{1 - \left(\frac{nb}{V}\right)} - \frac{an}{RTV}$.
 E : For real gases $Z \geq 1$.
 - S : $P(V - b) = RTe^{-a/RTV}$ is called Dieterici equation of state.
 E : Dieterici equation and van der Waals' equation both reduce to same expression of pressure at low densities.

19. S : At low temperature (say 0°C) the effect of attractive forces dominates for CO₂, CH₄ and N₂, whereas the molecular size effect dominates for H₂ and He to explain deviations.
 E : $Z > 1$ for H₂ and He, whereas $Z < 1$ for CO₂, CH₄ and N₂.
20. S : An ideal gas is not expected to show any cooling on free expansion.
 E : Ideal gas does not exist but is useful concept.
21. S : CO and N₂ have the same speed distribution at the same temperature.
 E : Both have same molar mass.
22. S : Speed distribution of O₂ at T K is same as for SO₂ at $2T$ K.
 E : $u \propto \sqrt{\frac{T}{M}}$.
23. S : Density of argon at STP is 1.7857 g litre.
 E : Specific gravity of argon at STP is 1.3842.
24. S : If the temperature of a sample of gas is increased from 25°C to 50°C, the volume of gas will increase by 100 per cent.
 E : The volume of the given mass of a gas is directly proportional to absolute temperature.
25. S : The pressure of wet gas is reduced to half, if its volume is doubled.
 E : Aqueous tension remains constant at constant pressure.
26. S : The value of van der Waals' constant 'a' is larger for NH₃ than for N₂.
 E : NH₃ shows H-bonding.
27. S : The pressure of fixed amount of an ideal gas is proportional to its temperature.
 E : Frequency of collisions and their impact both increase in proportion to the square root of temperature.
28. S : For H₂ and He, Z vs. P plots are linear throughout with positive slope.
 E : van der Waals' constant 'a' is minimum for these gases.
29. S : Compressibility factor 'Z' for van der Waals' gases at critical conditions shows more deviations than normal conditions, i.e., $Z = \frac{3}{8}$.
 E : At critical conditions van der Waals' equation is not accurate.
30. S : Rise in compressibility factor with increasing pressure is due to a .
 E : $Z = 1 + \frac{Pb}{RT}$, when $Z > 1$.
31. S : The gas on subjecting to Joule-Thomson effect gets heated if its temperature is less than its inversion temperature.
 E : Heating effect has Joule-Thomson coefficient -ve.
32. S : Liquefaction of a gas is a continuous process with increase in pressure below T_c .
 E : Liquefaction of a gas is a discontinuous process with increase in pressure below T_c .
33. S : At STP or any identical temperature and pressure, the volume occupied by a definite mass of any gas are identical.
 E : Equal mole of any monoatomic gas at same temperature have same average kinetic energy.
34. S : On heating a sample of gas collision frequency increases.
 E : Heat is produced by the collision of gas molecules against each other.
35. S : The coefficient of isothermal expansion at critical point is zero.
 E : $\left(\frac{\partial V_c}{\partial T_c}\right)_{P_c} = 0$
36. S : Compressibility factor 'Z' for H₂ is lower than CO₂.
 E : CO₂ has higher molar mass than H₂.
37. S : If two gases have same values 'b' but different values of 'a', then the gas having a larger value of 'a' will occupy lesser volume.
 E : The gas with a larger value of 'a' have higher force of attraction.
38. S : If two gases have same values of 'a' but different values of 'b' then the gas having lesser value of 'b' will show higher compressibility.
 E : The gas with smaller value of b will occupy lesser volume.
39. S : Poisson's ratio of atmospheric gases is approximately equal to 1.4.
 E : Gases present in atmosphere are mainly diatomic.
40. S : The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero. (IIT 2000)
 E : The volume occupied by the molecules of an ideal gas is zero.

ANSWERS (Statement Explanation Problems)

1. (b) $PV = nRT$
2. (b) At high pressure $Z = 1 + \frac{bP}{RT}$.
3. (b) At $T = T_c$, liquefaction is possible only at $P = P_c$.
4. (b) Above inversion temperature gas shows negative Joule-Thomson effect.
5. (c) Explanation is correct reason for statement.
6. (b) It is a fact, follow Maxwell distribution law.
7. (c) Explanation is correct reason for statement.
8. (b) Follow Maxwell distribution law.
9. (c) Explanation is correct reason for statement.
10. (c) $\left[P + \frac{a}{V^2}\right][V - b] = RT$; for H_2 and He, a is very small because of low molar mass. Thus, $PV = RT + Pb$. Now $Z = \frac{PV}{RT} = \left[1 + \frac{Pb}{RT}\right]$.
11. (d) $\frac{RT_c}{P_c \cdot V_c} = \frac{R \times 8a \times 27b^2}{27Rb \times a \times 3b} = \frac{8}{3}$
12. (b) a is more for C_6H_6 due to high molar mass of C_6H_6 .
13. (a) $PV + \frac{a}{V} = RT$
 $\therefore PV = RT - \frac{a}{V}$; Thus, $Z = \frac{PV}{RT} = \left[1 - \frac{a}{RTV}\right]$
14. (d) Average energy of diatomic molecule is $\frac{5}{2}RT$ at constant V
 $\therefore$ Average energy of diatomic molecule = $\frac{7}{2}RT$
 $\therefore$ Increase in internal energy = $\frac{7}{2}R(T+1) - \frac{7}{2}RT = \frac{7}{2}R$
15. (c) Explanation is correct reason for statement.
16. (d) Both are facts.
17. (d) —do—
18. (d) —do—
19. (c) Explanation is correct reason for statement.
20. (d) Both are facts.
21. (c) Explanation is correct reason for statement.
22. (c) —do—
23. (d) Density at STP

$$= \frac{\text{mass}}{V} = \frac{g \text{ mol}^{-1}}{24.4 \text{ L mol}^{-1}} = \frac{40}{22.4} = 1.7857$$

 Sp. gravity at STP = $\frac{\text{density of Ar at STP}}{\text{density of air at STP}}$

$$= \frac{1.7857}{1.29} = 1.3842$$
24. (b) $V \propto T$ (Kelvin)
25. (b) Saturated vapours do not obey gas laws.
26. (c) Explanation is correct reason for statement.
27. (d) Both are facts.
28. (c) Explanation is correct reason for statement.
29. (c) —do—
30. (b) The rise in compressibility factor with increase in pressure is due to b .
31. (b) If $T < T_i$ then cooling effect $\mu = +ve$
 If $T > T_i$ then heating effect $\mu = -ve$
32. (a) Follow Andrew's studies on CO_2 .
33. (b) Definite mole and not definite mass.
34. (a) Collisions are perfectly elastic, however kinetic energy of molecule changes but average kinetic energy remains unchanged.

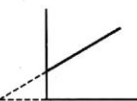
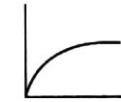
$$\left(\frac{\partial V_c}{\partial T_c}\right)_{P, n}; V_c, T_c, T_c \text{ are constant at critical conditions.}$$
35. (c) $\alpha = \frac{\left(\frac{\partial V_c}{\partial T_c}\right)_{P, n}}{V_c}$; V_c, T_c, T_c are constant at critical conditions.
36. (b) Z for $H_2 > Z$ for CO_2 .
37. (c) Explanation is correct explanation for statement.
38. (c) —do—
39. (c) Explanation is correct reason for statement
 $\gamma = \frac{C_p}{C_v} = 1.4$ for diatomic gases. Atmosphere mainly contains N_2 and O_2 .
40. (a) $\Delta U = q - w$. For isothermal expansion, $\Delta U = 0$ and $w = 0$ because $w = P\Delta V$ (at $P = 0$)
 Volume occupied by the molecules of ideal gas is not zero but negligible.

MATCHING TYPE PROBLEMS

Type I : Only One Match Possible

- | 1. List-A | List-B |
|---------------------------------|------------------------------|
| A. Kinetic energy of 1 mole gas | 1. $\sqrt{2 KE / M}$ |
| B. Root mean square speed | 2. $\frac{3PV}{2}$ |
| C. Average speed | 3. $\sqrt{\frac{8P}{\pi d}}$ |
| D. Most probable speed | 4. $\sqrt{4 KE / 3M}$ |

- | 2. List-A | List-B |
|--------------------------|----------------------|
| A. Boyle's temperature | 1. $\frac{8a}{27Rb}$ |
| B. Reduced temperature | 2. $\frac{a}{Rb}$ |
| C. Inversion temperature | 3. $\frac{2a}{Rb}$ |
| D. Critical temperature | 4. $\frac{T}{T_c}$ |

- | 3. List-A | List-B |
|--|--|
| A. PT vs. T^2 plot for ideal gas at constant n and V (in K) | 1.  |
| B. V vs. $\frac{1}{P^2}$ graph for ideal gas at constant n and T | 2.  |
| C. VT vs. T^2 graph for ideal gas at constant n and P | 3.  |
| D. V vs. $\frac{1}{T}$ graph for ideal gas at constant P and n | 4.  |
| E. V vs. P graph for ideal gas at constant T and n | |
| F. $\frac{1}{V^2}$ vs. P graph for ideal gas at constant T and n | |

Type II : More Than One Match Are Possible

- | 4. List-A | List-B |
|-------------------------------|----------------------------|
| A. Vacuum technology | 1. Television tube |
| B. Critical temperature | 2. Semiconductor |
| C. Andrew's studies on CO_2 | 3. Liquefaction of gases |
| D. Dalton's law | 4. $T_c = \frac{8a}{27Rb}$ |
| E. Graham's law | 5. Moist gases |
| F. Vacuum | 6. Aqueous tension |
| | 7. Effusion of gases |
| | 8. Diffusion of gases |

- | 5. List-A | List-B |
|---|-----------------------|
| A. $\left(\frac{\partial T}{\partial P}\right)_H$ | 1. C_v |
| B. $\left(\frac{\partial V}{\partial P}\right)_T$ | 2. C_p |
| C. $\left(\frac{\partial H}{\partial T}\right)_P$ | 3. $\mu_{J.T.}$ |
| D. $\left(\frac{\partial U}{\partial V}\right)_T$ | 4. Zero for ideal gas |
| E. $\left(\frac{\partial U}{\partial T}\right)_V$ | 5. $-\frac{V}{P}$ |

- | 6. List-A | List-B |
|---|----------------------------------|
| A. H_2 (gas) at $P = 200$ atm, $T = 273$ K | 1. $Z \neq 1$ |
| B. H_2 (gas) at $P \rightarrow 0$, $T = 273$ K | 2. Attractive forces predominate |
| C. CO_2 gas at $P = 1$ atm, $T = 273$ K | 3. $PV = nRT$ |
| D. Real gas with large molar volume | 4. $P(V - nb) = nRT$ |

- | 7. List-A | List-B |
|---|------------|
| A. H_2 and He | 1. $Z > 1$ |
| B. CO_2 | 2. $Z < 1$ |
| C. For a gas other than H_2 and He at T_B | 3. $Z = 1$ |
| D. For a gas when only repulsive forces predominate | |

ANSWERS

- | | |
|---|-------------------------------|
| 1. A-2; B-1; C-3; D-4 | 5. A-3, 4; B-5; C-2; D-4; E-1 |
| 2. A-2; B-4; C-3; D-1 | 6. A-1, 4; B-3; C-1, 2; D-3 |
| 3. A-2; B-4; C-2; D-3; E-3; F-1 | 7. A-1; B-1, 3; C-2; D-1 |
| 4. A-1, 2; B-3, 4; C-3; D-5, 6; E-7, 8; F-1, 2, 7 | |