

## STATES OF MATTER

## GASEOUS STATE

## INTRODUCTION

- \* We live at the bottom of an ocean of air whose composition by volume is roughly 78 percent  $N_2$ , 21 percent  $O_2$ , and 1 percent other gases, including  $CO_2$ .
- \* We will focus generally on the behaviour of substances that exist as gases under normal atmospheric conditions, which are defined as  $25^\circ C$  and 1 atmosphere (atm) pressure.
- \* Only 11 elements are gases under normal atmospheric conditions.
- \* Hydrogen, nitrogen, oxygen, fluorine, and chlorine exist as gaseous diatomic molecules. Another form of oxygen, ozone ( $O_3$ ), is also a gas at room temperature. All the elements in Group 18, the noble gases, are monatomic gases: He, Ne, Ar, Kr, Xe, and Rn.
- \* In gases, the distances between molecules are so great (compared with their diameters) that at ordinary temperatures and pressures (say,  $25^\circ C$  and 1 atm), there is no appreciable interaction between the molecules. Because there is a great deal of empty space in a gas—that is, space that is not occupied by molecules—gases can be readily compressed.
- \* The lack of strong forces between molecules also allows a gas to expand to fill the volume of its container.
- \* Furthermore, the large amount of empty space explains why gases have very low densities under normal conditions.
- \* Liquids and solids are quite a different story. The principal difference between the condensed states (liquids and solids) and the gaseous state is the distance between molecules. In a liquid, the molecules are so close together that there is very little empty space. Thus, liquids are much more difficult to compress than gases, and they are also much denser under normal conditions. Molecules in a liquid are held together by one or more types of attractive forces.
- \* A liquid also has a definite volume, because molecules in a liquid do not break away from the attractive forces.
- \* The molecules can, however, move past one another freely, and so a liquid can flow, can be poured, and assumes the shape of its container.
- \* In a solid, molecules are held rigidly in position with virtually no freedom of motion. Many solids are characterized by long-range order; that is, the molecules are arranged in regular configurations in three dimensions. There is even less empty space in a solid than in a liquid. Thus, solids are almost incompressible and possess definite shape & volume.
- \* With very few exceptions (water being the most important), the density of the solid form is higher than that of the liquid form for a given substance.

- \* It is not uncommon for two states of a substance to coexist. An ice cube (solid) floating in a glass of water (liquid) is a familiar example. Thus, our glass of ice water contains both the solid phase and the liquid phase of water.

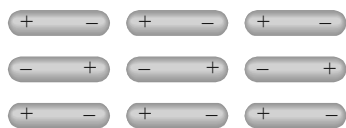
## INTERMOLECULAR FORCES

- \* Intermolecular forces are attractive forces between molecules.
- \* In contrast to intermolecular forces, intramolecular forces hold atoms together in a molecule.
- \* Intramolecular forces stabilize individual molecules, whereas intermolecular forces are primarily responsible for the bulk properties of matter (for example, melting point and boiling point).
- \* Generally, intermolecular forces are much weaker than intramolecular forces. Much less energy is usually required to evaporate a liquid than to break the bonds in the molecules of the liquid.
- \* For example, it takes about 41 kJ of energy to vaporize 1 mole of water at its boiling point; but about 930 kJ of energy are necessary to break the two O–H bonds in 1 mole of water molecules.
- \* The boiling points of substances often reflect the strength of the intermolecular forces operating among the molecules.
- \* At the boiling point, enough energy must be supplied to overcome the attractive forces among molecules before they can enter the vapour phase. If it takes more energy to separate molecules of substance A than of substance B because A molecules are held together by stronger intermolecular forces, then the boiling point of A is higher than that of B.
- \* The same principle applies also to the melting points of the substances. In general, the melting points of substances increase with the strength of the intermolecular forces.
- \* The different types of intermolecular forces, like **Dipole-dipole, dipole-induced dipole, and dispersion forces** make up **van der Waals forces**, after the Dutch physicist Johannes van der Waals.
- \* Ions and dipoles are attracted to one another by electrostatic forces called **ion-dipole forces**, which are not van der Waals forces.
- \* **Hydrogen bonding** is a particularly strong type of dipole-dipole interaction.

## Dipole-dipole forces :

- \* Dipole-dipole forces are attractive forces between polar molecules, that is, between molecules that possess dipole moments.
- \* Their origin is electrostatic, and they can be understood in terms of Coulomb's law.

- \* The larger the dipole moment, the greater the force. Figure shows the orientation of polar molecules in a solid.

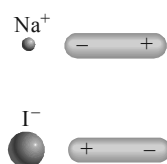


**Figure :** Molecules that have a permanent dipole moment tend to align with opposite polarities in the solid phase for maximum attractive interaction.

- \* In liquids, polar molecules are not held as rigidly as in a solid, but they tend to align in a way that, on average, maximizes the attractive interaction.
- \* Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to  $1/r^3$  and that between rotating polar molecules is proportional to  $1/r^6$ , where  $r$  is the distance between polar molecules.

#### Ion-Dipole Forces :

- \* Coulomb's law also explains ion-dipole forces, which attract an ion (either a cation or an anion) and a polar molecule to each other (figure).

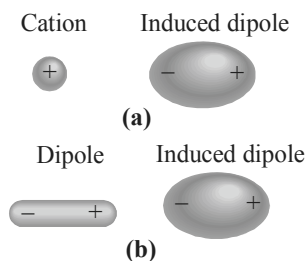


**Figure :** Two types of ion-dipole interaction.

- \* The strength of this interaction depends on the charge and size of the ion and on the magnitude of the dipole moment and size of the molecule.
- \* The charges on cations are generally more concentrated, because cations are usually smaller than anions. Therefore, a cation interacts more strongly with dipoles than does an anion having a charge of the same magnitude.

#### Dipole-induce dipole forces

- \* If we place an ion or a polar molecule near an atom (or a nonpolar molecule), the electron distribution of the atom (or molecule) is distorted by the force exerted by the ion or the polar molecule, resulting in a kind of dipole.



**Figure :** (a) Distortion caused by the approach of a cation. (b) Distortion caused by the approach of a dipole.

- \* The dipole in the atom (or nonpolar molecule) is said to be an induced dipole because the separation of positive and negative charges in the atom (or nonpolar molecule) is due to the proximity of an ion or a polar molecule.

- \* The attractive interaction between an ion and the induced dipole is called **ion-induced dipole interaction**, and the attractive interaction between a polar molecule and the induced dipole is called **dipole-induced dipole interaction**.
- \* The likelihood of a dipole moment being induced depends not only on the charge on the ion or the strength of the dipole but also on the **polarizability** of the atom or molecule—that is, the ease with which the electron distribution in the atom (or molecule) can be distorted.
- \* Generally, the larger the number of electrons and the more diffuse the electron cloud in the atom or molecule, the greater its polarizability.
- \* By diffuse cloud we mean an electron cloud that is spread over an appreciable volume, so that the electrons are not held tightly by the nucleus.
- \* Polarizability allows gases containing atoms or nonpolar molecules (for example, He and  $N_2$ ) to condense.
- \* Interaction energy is proportional to  $1/r^6$  where  $r$  is the distance between two molecules.
- \* Hydrogen bond is a special case of dipole-dipole interaction.

#### Dispersion forces or London forces:

- \* Dispersion forces are attractive forces that arise as a result of temporary dipoles induced in atoms or molecules.
- \* At very low temperatures (and reduced atomic speeds), dispersion forces are strong enough to hold He atoms together, causing the gas to condense.
- \* A quantum mechanical interpretation of temporary dipoles was provided by the German physicist Fritz London in 1930.
- \* London showed that the magnitude of this attractive interaction is directly proportional to the polarizability of the atom or molecule.
- \* As we might expect, dispersion forces may be quite weak. This is certainly true for helium, which has a boiling point of only 4.2 K, or  $-269^\circ\text{C}$ . (Note that helium has only two electrons, which are tightly held in the 1s orbital. Therefore, the helium atom has a low polarizability.)
- \* Dispersion forces, which are also called **London forces**, usually increase with molar mass because molecules with larger molar mass tend to have more electrons, and dispersion forces increase in strength with the number of electrons.
- \* In many cases, dispersion forces are comparable to or even greater than the dipole-dipole forces between polar molecules.
- \* For example, let us compare the boiling points of  $\text{CH}_3\text{F}$  ( $-78.4^\circ\text{C}$ ) and  $\text{CCl}_4$  ( $76.5^\circ\text{C}$ ). Although  $\text{CH}_3\text{F}$  has a dipole moment of 1.8 D, it boils at a much lower temperature than  $\text{CCl}_4$ , a nonpolar molecule.
- \*  $\text{CCl}_4$  boils at a higher temperature simply because it contains more electrons. As a result, the dispersion forces between  $\text{CCl}_4$  molecules are stronger than the dispersion forces plus the dipole-dipole forces between  $\text{CH}_3\text{F}$  molecules.
- \* Interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e.,  $1/r^6$  where  $r$  is the distance between two particles).

- \* These forces are important only at short distances ( $\sim 500\text{pm}$ ) and their magnitude depends on the polarizability of the particle.

**Note :** Dipole-dipole forces are stronger than the London forces but is weaker than ion-ion interaction.

### THE GASEOUS STATE

- \* When the molecular forces of attraction between the particles of a matter are minimum, the particles exist in a state known as gaseous state or a state of matter in which molecules are far away from each other and free to move in available space is called gaseous state.
- \* All gases have the following physical characteristics:
  - Gases assume the volume and shape of their containers.
  - Gases are the most compressible of the states of matter.
  - Gases will mix evenly and completely when confined to the same container.
  - Gases have much lower densities than liquids and solids.

### Parameters of Gases :

- \* The characteristics of gases are described in terms of four measurable parameters and it is also called as measurable properties of gases which are (a) Mass (b) Volume (c) Pressure (d) Temperature

- (a) **Mass (m)** – The mass of a gas is denoted by ‘m’ which is related to the number of moles ‘n’.

$$n \text{ (number of moles)} = \frac{m \text{ (mass in grams)}}{M \text{ (Molar mass)}}. \text{ So, } m = n \times M$$

- (b) **Volume V :**

- \* Gases occupy whole space available to them. The volume occupied by a gas is simply the volume of container in which it is filled.
- \* The volume of a gas is denoted by ‘V’ and it is measured in units of litre of cubic metre ( $\text{m}^3$ ) or  $\text{cm}^3$  or  $\text{dm}^3$ .
- \* 1 litre =  $1 \text{ dm}^3 = 1000 \text{ cm}^3 = 1000 \text{ ml}$

- (c) **Temperature (T) :**

- \* The temperature of a gas is denoted by ‘T’ and it is measured in the unit of kelvin (K).
- \* Other units of temperature are  $^{\circ}\text{C}$ ,  $^{\circ}\text{F}$ ,  $^{\circ}\text{R}$
- \*  $\text{K} = ^{\circ}\text{C} + 273.15$

$$\frac{x^{\circ}\text{C}}{5} = \frac{(y^{\circ}\text{F} - 32)}{9}$$

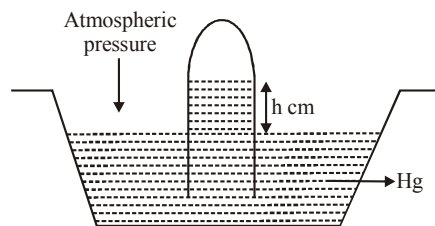
- (d) **Pressure (P) :**

- \* It is force acting per unit area. A confined gas exerts uniform pressure on the walls of its container in all the direction.

$$P \text{ (Pressure)} = \frac{F \text{ (Force)}}{A \text{ (Area)}}$$

- \* It is denoted by ‘P’ and specified in pascal ( $p_a$ )
- \* Other units of pressure are atm, cm, Hg, mmHg,  $\text{N/m}^2$ , bar, torr.
- \* Atmospheric pressure is the pressure exerted by Earth’s atmosphere
- \*  $1 \text{ atm} = 76 \text{ cm Hg} = 760 \text{ mm Hg} = 1.013 \times 10^5 \text{ N/m}^2$   
 $= 1.013 \times 10^5 p_a = 1.013 \text{ bar} = 760 \text{ torr}.$

- \* Pressure exerted by a gas is due to kinetic energy of the gases molecules.
- \* K.E. of the gas molecule increases, as the temperature is increased so, pressure of a gas is directly proportional to temperature.  $P \propto T$ .
- \* **Barometer:** The instrument used for the measurement of atmospheric pressure is called Barometer. It consists inverted tube filled with mercury in a dish of mercury. The height of the mercury column measure the atmospheric pressure at that place.



$$\begin{aligned} \text{Volume of Hg} &= \text{Area} \times \text{Height} = A \times h \\ \text{Mass of Hg} &= \text{Volume} \times \text{Density} = A \times h \times d \\ \text{Force due to mercury} &= \text{Mass} \times g = A \times h \times d \times g \end{aligned}$$

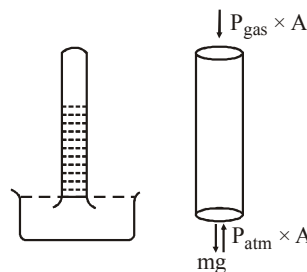
$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{A \times h \times d \times g}{A} = hdg$$

$$P = hdg \Rightarrow h = \frac{P}{dg}$$

$$\begin{aligned} d_{\text{Hg}} &= 13.6 \text{ g/ml} = 13.6 \times 10^3 \text{ kg/m}^3 \\ \text{If } P &= 1 \text{ atm} = 1.01325 \times 10^5 \text{ Pascal} \end{aligned}$$

$$h = \frac{1.01325 \times 10^5}{13.6 \times 10^3 \times 9.8} = 0.76 \text{ m} = 760 \text{ cm} = 760 \text{ mm}.$$

**Faulty Barometer:** An ideal barometer will show a correct reading only if the space above the mercury column is vacuum, but in case if some gas column is trapped in the space above the mercury column, then the barometer is classified as a faulty barometer. The reading of such a barometer will be less than the true pressure.



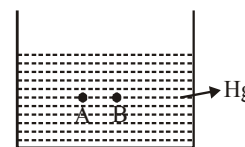
For such a faulty barometer

$$P_0 A = Mg + P_{\text{gas}} A; P_0 = hdg + P_{\text{gas}} \text{ or } hdg = P_0 - P_{\text{gas}}$$

**Note :**

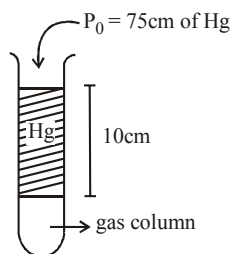
1. Pressure in liquid is independent on cross section area. It only dependent upon height of column.
2. Pressure at all the points lying on the same horizontal level are always same.

$$\begin{aligned} P_A &= P_B \\ P_A - P_B &= 0 \end{aligned}$$



**Example 1 :**

Find the pressure of the trapped gas.



**Sol.** Total pressure of gas column = 75 + 10 = 85 cm of Hg.

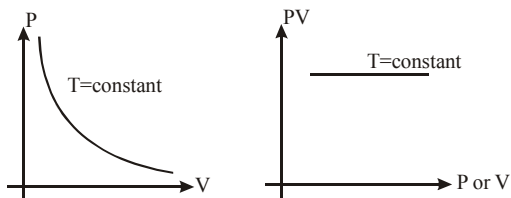
**GAS LAWS**

The certain laws which relate the four parameters are called gas laws.

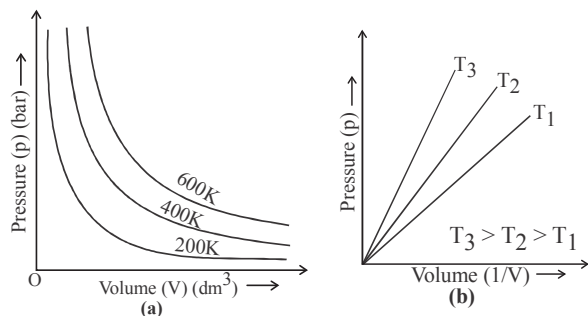
**Boyle's law :**

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

\* Mathematically,  $P \propto \frac{1}{V}$  or  $PV = \text{constant}$



\* Curves corresponding to a different constant temperature are called **isotherm**.



**Figure (a) Graph of pressure, p vs. Volume, V of a gas at different temperatures. (b) Graph of pressure of a gas, p vs. 1/V**

**Example 2 :**

A gas is present at a pressure of 2 atm. What should be the increase in pressure so that the volume of the gas can be decreased to 1/4<sup>th</sup> of the initial value if the temperature is maintained constant.

**Sol.**  $PV = \text{constant}$  for a given mass of gas at constant pressure  
 $\Rightarrow P_1V_1 = P_2V_2$ ;  $P_1 = 2 \text{ atm}$ ;  $V_1 = V$ ;  $V_2 = V/4$ ;  $P_2 = ?$

Now,  $2 \times V = P_2 \times \frac{V}{4} \Rightarrow P_2 = 8 \text{ atm}$

$\therefore$  Pressure should be increased from 2 to 8 atm.

$\therefore$  Total increase = 8 – 2 = 6 atm.

**Charle's law :**

\* Charle's law states that at constant pressure, the volume of a given mass of a gas is directly proportional to its absolute temperature. (Absolute temperature = °C + 273.15)

\* Mathematically –  $V \propto T$  (at constant pressure)  
 $V = \text{volume of gas}$ ,  $T = \text{Absolute temperature}$

$$V = KT \text{ or } \frac{V}{T} = K$$

\* Hence, if the volume of a gas of mass is  $V_1$  at temperature  $T_1$  changes to  $V_2$  at  $T_2$ , pressure remaining constant then

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant} \text{ or } \log V - \log T = \text{constant}$$

\* For each degree change of temperature the volume of sample of a gas changes by the fraction of 1/273.15 of its

volume at 0°C. So  $V_t = V_0 \left[ \frac{273.15 + t}{273.15} \right]$

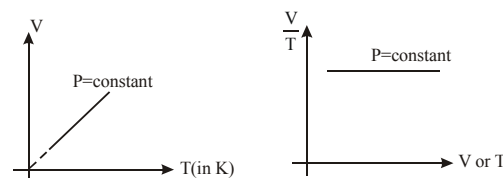
This equation is called charles-gay-lussac equation.

where,  $V_t = \text{volume of gas at temperature } t^\circ\text{C}$

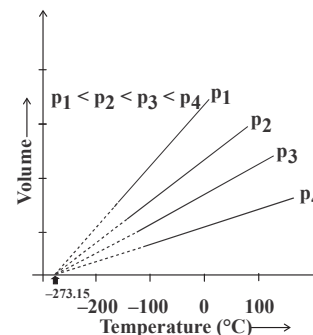
$V_0 = \text{volume of gas at } 0^\circ\text{C temperature}$

$t = \text{temperature in } ^\circ\text{C}$

**Graphical representation**



\* Curves corresponding to a different constant pressure are called **isobar**.



**Figure : Volume vs Temperature ( °C) graph**

**Example 3 :**

Volume of given amount of a gas at 57°C and constant pressure is 425.8 cm<sup>3</sup>. If the temperature is decreased to 37°C at constant pressure, then the volume will be

**Sol.** According to charles law,  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ ;  $V_1 = 425.8 \text{ cm}^3$ ,  $V_2 = ?$

$T_1 = 273 + 57 = 330 \text{ K}$  ;  $T_2 = 273 + 37 = 310 \text{ K}$

$$V_2 = \frac{425.8 \times 310}{330} = 400 \text{ cm}^3$$

**Gay-Lussac's Law or Amonton's Law :**

- \* It states that at constant volume, the pressure of a given mass of a gas is directly proportional to its absolute temperature.
- \* Mathematically –  $P \propto T$  (at constant volume)  
Where, P = pressure of gas, T = Absolute temperature

$$P = KT \quad \text{or} \quad \frac{P}{T} = K$$

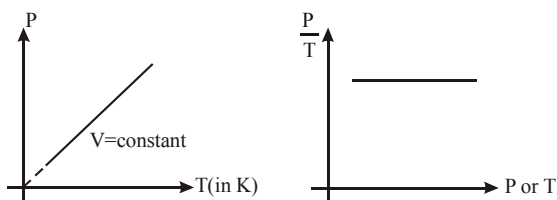
- \* Hence, if the pressure of a gas is  $P_1$  at temperature  $T_1$  changes to  $P_2$  at  $T_2$ , volume remaining constant.

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

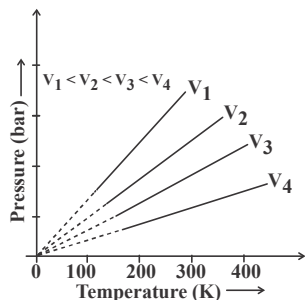
$$\log P - \log T = \text{constant} ; P_t = P_0 \left( 1 + \frac{t}{273.15} \right)$$

Where  $P_t$  = Pressure of gas at  $t^\circ\text{C}$ ,

$P_0$  = Pressure of gas at  $0^\circ\text{C}$ ,  $t$  = Temperature in  $^\circ\text{C}$

**Graphical representation -**

- \* Curves corresponding to a different constant volume are called **isochore**.



**Figure : Pressure vs temperature (K) graph (Isochores) of a gas.**

The temperature of a certain mass of a gas is doubled. If initially the gas is at 1 atm pressure. Find the % increase in pressure?

$$\text{Sol. } \frac{P_1}{T_1} = \frac{P_2}{T_2} ; \frac{1}{T} = \frac{P_2}{2T} ; \% \text{ increase} = \frac{2-1}{1} \times 100 = 100\%$$

**AVOGADRO'S LAW**

- \* At the same volume, pressure, and temperature, samples of different gases have the same number of molecules but different masses.
- \*  $V \propto n$  (At constant temperature & pressure)  
Where, V = volume, n = no of molecules
- \* **Loschmidt number** : It the number of molecules present in the volume of a gas at S.T.P. Its value is  $2.617 \times 10^{19}$  per c.c.

**IDEAL GAS EQUATION**

- \* It correlates all the four parameters of a gas.
- \* It is the combination of Boyle's, Charle's and Avogadro's law.

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

The equation is called as ideal gas equation.

Where, n = number of moles of the gas,  
m = mass of the gas, M = Mol. wt. of the gas,  
R = Molar gas constant.

- \* For 1 mole of gas  $n = 1$  ;  $PV = RT$

$$\text{So, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = R \quad \text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Where  $P_1, V_1, T_1$  are the initial pressure, volume and temperature and  $P_2, V_2, T_2$  are final.

The above equation is called as ideal gas equation.

- \* The unit of R is the unit of work or energy per degree per

$$\text{mole as : } R = \frac{PV}{nT} = \frac{\text{Pressure} \times \text{volume}}{\text{mole} \times \text{Temperature}}$$

$$R = \frac{\frac{\text{Force}}{\text{Area}} \times \text{volume}}{\text{mole} \times \text{Temperature}} = \frac{\text{force} \times \text{length}}{\text{mole} \times \text{temperature}}$$

$$R = \frac{\text{work(energy)}}{\text{mole} \times \text{temperature}}$$

- \* Numerical values of R in different units -

- $R = 0.0821 \text{ litre atm deg}^{-1} \text{ mole}^{-1}$
- $R = 62.4 \text{ litres mm deg}^{-1} \text{ mole}^{-1}$
- $R = 8.314 \times 10^7 \text{ ergs deg}^{-1} \text{ mole}^{-1}$
- $R = 82.05 \text{ cc atm deg}^{-1} \text{ mole}^{-1}$
- $R = 2 \text{ cal. deg}^{-1} \text{ mole}^{-1}$
- $R = 8.314 \text{ J K}^{-1} \text{ mole}^{-1}$

- \* Suppose we have 1.000 mol of an ideal gas at 1.000 atm  $0.00^\circ\text{C}$  and (273.15 K).

According to the ideal-gas equation, the volume of the

$$\text{gas is } V = \frac{nRT}{P} = \frac{(1.000 \text{ mol}) (0.0821 \text{ L-atm/mol-K}) \times (273.15 \text{ K})}{1.000 \text{ atm}} = 22.4 \text{ L}$$

The conditions  $0^\circ\text{C}$  and 1 atm are referred to as **standard temperature and pressure (STP)**.

The volume occupied by 1 mol of ideal gas at STP, 22.4 L, is known as the **molar volume** of an ideal gas at STP.

**Ideal gas equation in terms of density**

- \* For an ideal gas  $PV = nRT$  or  $PV = \frac{W}{M} RT$ ,

where w = mass of the gas in gms and  
M = Molecular weight in gms.

$$\therefore PM = \frac{W}{V} RT \quad \text{or} \quad PM = d RT,$$

(where d is the density of the gas =  $w/V$ )

$$\therefore d = \frac{PM}{RT}$$

$$(i) \frac{d_1 T_1}{P_1} = \frac{d_2 T_2}{P_2}$$

(for same gas at different temperature and pressure)

$$(ii) \frac{d_1}{d_2} = \frac{M_1}{M_2} \text{ (for different gases at same temperature \&}$$

pressure), (Where d = density of gas)

#### Example 5 :

Some spherical balloons each of volume 2 litre are to be filled with hydrogen gas at one atm & 27°C from a cylinder of volume 4 litres. The pressure of the H<sub>2</sub> gas inside the cylinder is 20 atm at 127°C. Find number of balloons which can be filled using this cylinder. Assume that temperature of the cylinder is 27°C.

$$\text{Sol. No. of moles of gas taken initially} = \frac{20 \times 4}{R \times 400} = 2.43 \text{ L}$$

$$\text{No. of moles of gas left in cylinder} = \frac{1 \times 4}{R \times 300} = 0.162 \text{ L}$$

$$\text{No. of moles of gas to be filled in balloons} \\ = 2.43 - 0.162 = 2.268$$

Let we have n balloons that we can fill

No. of moles of gas that can be filled in 1 balloon

$$= \frac{1 \times 2}{0.082 \times 300} = 0.081$$

$$\therefore 0.081 \times n = 2.268 ; n = 28 \text{ balloons}$$

#### DALTON'S LAW OF PARTIAL PRESSURE

\* According to this law, when two or more than two chemically inert gases are kept in a closed container, the total pressure exerted by the gaseous mixture is equal to the sum of the partial pressures of individual gases i.e.

$$P = P_1 + P_2 + P_3 + \dots + P_n$$

\* Let n<sub>1</sub> & n<sub>2</sub> be the number of moles of two inert gases A and B which is filled in a container of volume 'V' at temperature T. So the total pressure of container 'P' may be calculated as

$$PV = (n_1 + n_2) RT \quad \dots\dots (i)$$

Partial pressure of individual gas calculates at

$$P_A V = n_1 RT \quad \dots\dots (ii)$$

$$P_B V = n_2 RT \quad \dots\dots (iii)$$

On the addition of eq. (ii) & (iii) we get -

$$(P_A + P_B) V = (n_1 + n_2) RT \quad \dots\dots (iv)$$

On the comparison of eq. (i) & (iv)

$$P = P_A + P_B$$

Dividing by equation (ii) by (i), we get

$$\frac{P_A}{P} = \frac{n_1}{n_1 + n_2} = x_A ; P_A = x_A \times P$$

where x<sub>A</sub> = mole fraction of 'A'

Similarly dividing (iii) by (i), we get P<sub>B</sub> = x<sub>B</sub> × P

So, Partial pressure of a component = mole fraction × total pressure

#### Applications of Dalton's Law of Partial pressure

(a) Mole fraction of a gas in a mixture of gas

$$= \frac{\text{partial pressure of gas}}{\text{Total pressure of the mixture of gas}}$$

(b) % of a gas in a mixture =  $\frac{\text{partial pressure of gas}}{\text{Total pressure}} \times 100$

(c) Pressure of dry gas which is collected over the water is -

$$P_{\text{Total}} = P_{\text{moist air}} = P_{\text{dry gas}} + P_{\text{water vapour}}$$

(Note : P<sub>water vapour</sub> is called aqueous tension)

so P<sub>dry gas</sub> = Total measured pressure – Aqueous tension

(Note : Aqueous tension is directly proportional to absolute temperature)

#### Limitations of Dalton's law of partial pressure

(a) It is applicable only for inert gases like N<sub>2</sub> and O<sub>2</sub>, N<sub>2</sub> and Cl<sub>2</sub> etc.

(b) It is not applicable for chemically reactive gases like H<sub>2</sub> and Cl<sub>2</sub>, Co and Cl<sub>2</sub> etc.

#### Example 6 :

A gaseous mixture of 0.336 gram N<sub>2</sub> and 11.2 gram litre O<sub>2</sub> is taken at NTP in a ten-litre flask at 27°C. Calculate the partial pressure and total pressure of each gas.

$$\text{Sol. Mole of N}_2 = \frac{\text{Mass of N}_2}{\text{Molecular mass of N}_2} = \frac{0.336}{28} = 0.012 \text{ mole}$$

$$\text{Mole of O}_2 = \frac{11.2}{22.4} = 0.5 \text{ mole}$$

Partial pressure of N<sub>2</sub>

$$P_{N_2} = \frac{nRT}{V} = \frac{0.012 \times 0.0821 \times 300}{10} = 0.0296 \text{ atm}$$

$$\text{Partial pressure of O}_2, P_{O_2} = \frac{0.05 \times 0.0821 \times 300}{10}$$

$$\text{Total pressure} = 0.0296 + 1.2315 = 1.2611 \text{ atm}$$

#### GRAHAM'S LAW OF DIFFUSION OR EFFUSION

\* **Diffusion** : It is the ability of a gas to mix spontaneously and to form a homogenous mixture.

\* **Effusion** : It is a process in which a gas is allowed to escape under pressure through a fine orifice from closed container.

\* **LAW** : This law was proposed by Thomas Graham. According to this law, at constant temperature, the rate of diffusion or effusion of a gas is inversely proportional to the square root of its density, and directly proportional to pressure difference.

$$\text{Rate of diffusion (r)} \propto \frac{P}{\sqrt{d}} ; \frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{d_2}{d_1}}$$

If pressure is constant,  $\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$

Where  $r_1$  &  $r_2$  are rates of diffusion of two gases and  $d_1$  &  $d_2$  are densities.

$\therefore 2 \times \text{vapour density} = \text{Molecular mass}$

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

Where  $M_1$  &  $M_2$  are the molecular masses of two gases.

$$\text{Rate of diffusion} = \frac{\text{Volume of gas diffused}}{\text{Time taken for diffusion}}$$

### Applications of graham's law of diffusion

\* In the detection of marsh gas in mines.

\* Separation of isotopes

\* Determination of density and molecular mass of gases.

**Note :** It should be noted that the rate of diffusion or effusion actually depends on pressure difference of the gas and not simply on its pressure. Moreover the pressure is to be measured for given gas only i.e. if a container holds [He] at a pressure of 0.1 atm and if a small pin-hole is made in the container and if the container is placed in a room, then the rate of effusion of He gas from the container to outside depends only on its pressure difference, which is 0.1 atm (as there is no He in the atmosphere). This implies that the diffusion of a gas is not dependent on the diffusion of any other gas.

### Example 7 :

Pure  $O_2$  diffuses through an aperture in 224 seconds, whereas mixture of  $O_2$  and another gas containing 80%  $O_2$  diffuses from the same in 234 sec. under similar condition of pressure and temperature. What is molecular wt. of gas?

**Sol.** The gaseous mixture contains 80%  $O_2$  and 20% gas

$\therefore$  Average molecular weight of mixture

$$(M_{\text{mix}}) = \frac{32 \times 80 + 20 \times m_{\text{mix}}}{100} \quad \dots\dots\dots (1)$$

Now, for diffusion of gaseous mixture and pure  $O_2$

$$\frac{r_{O_2}}{r_m} = \sqrt{\frac{M_{\text{mix}}}{M_{O_2}}} \quad \text{or} \quad \frac{V_{O_2}}{V_{\text{mix}}} \times \frac{t_{\text{mix}}}{t_{O_2}} = \sqrt{\frac{M_{\text{mix}}}{32}}$$

$$\text{or} \quad \frac{1}{224} \times \frac{234}{1} = \sqrt{\frac{M_{\text{mix}}}{32}} \quad \dots\dots\dots (2)$$

$\therefore M_{\text{mix}} = 34.92$

By eq. (1) and (2) mol weight of gas (m) = 46.6

### CONNECTING CONTAINERS

1. When we are connecting two or more containers then the movement of any component of gas occurs in other container till the final pressure of the component in all the container become equal (that means partial pressure becomes equal).

2. To calculate composition of gaseous mixture in any container, we will use diffusion.

### Example 8 :

A 10 litre container of 1 mole of gas at 300 K. It is connected to another container having volume 40 litre and is initially at 300 K. The nozzle connecting two containers is opened for a long time and once the movement of gas stopped, the larger container was heated to a temperature of 600 K. Calculate (a) Moles and pressure of gas in both the containers before heating. (b) Moles and pressure in two containers after heating. (Assume that initially the larger container is completely evacuated)

**Sol.** (a) Before heating:  $PV = nRT$

$$\frac{(1-x)R \times 300}{10} = \frac{x \times R \times 300}{40}; \quad x = 0.8 \text{ moles}$$

$$\text{Pressure} = \frac{x \times R \times T}{V} = \frac{0.8 \times R \times 300}{40} = 0.492 \text{ atm}$$

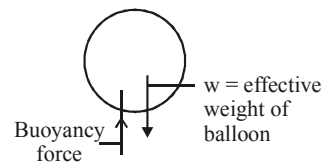
$$(b) \text{ After heating : } \frac{(1-x_1)R \times 300}{10} = \frac{x_1 \times R \times 600}{40}$$

$x_1 = 0.67$  moles, Given  $T_1 = 600$  K

$$\text{Pressure} = \frac{x_1 \times R \times T_1}{V} = \frac{0.67 \times 0.821 \times 600}{40} = 0.821 \text{ atm}$$

### PAYLOAD OF BALLOON

Payload of a balloon is defined as maximum weight which a balloon can carry with it upward direction.



$V$  = Volume of Balloon,  $d_{\text{out}}$  = density of outside air

$d_{\text{in}}$  = density of gas inside,  $m$  = mass of balloon

$$\text{Payload} = [\text{Buoyancy force}] - [\text{effective wt. of balloon}]$$

$$= d_{\text{out}} \times V \times g - [d_{\text{in}} V \times g + mg]$$

### Example 9 :

Calculate the payload of balloon of diameter 20 meter & weight 100 kg. If it is filled with He at 1.0 atm and 27°C. Density of air is  $1.2 \text{ kgm}^{-3}$ . [ $R = 0.82 \text{ dm}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$ ]

**Sol.** Weight of balloon = 100 kg =  $10 \times 10^4$  g

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

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

Weight of gas (He) in balloon

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

Total weight of gas and balloon

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

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

$$\begin{aligned} \therefore \text{Payload} &= \text{wt. of air displaced} \\ &\quad - (\text{wt. of balloon} + \text{wt. of gas}) \\ \therefore \text{Payload} &= 502.8 \times 10^4 - 7813 \times 10^4 = 424 \times 10^4 \text{ g} \\ &= 4.2467 \times 10^6 \text{ g} \end{aligned}$$

**TRY IT YOURSELF-1**

- Q.1** A sample of hydrogen gas occupies 320 cm<sup>3</sup> at STP. Calculate its volume when the temperature is raised to 47°C and pressure is reduced to 600mm of Hg.
- Q.2** If 246gm of a triatomic ideal gas having only one type of atoms is found to occupy 44.8 L at 2 atm and 546 K then atomic weight of the element will be –  
(A) 246 (B) 123 (C) 41 (D) 82
- Q.3** How many moles of oxygen are present in a 500cm<sup>3</sup> sample of oxygen gas at a pressure of 760mm of Hg and a temperature of 27°C?
- Q.4** If 200mL of N<sub>2</sub> at 25°C and 250mm Hg mixed with 350mL of H<sub>2</sub> gas at 25°C and 300mm Hg and enclosed in a vessel of 300mL, what will be the final pressure of the mixture?
- Q.5** A fluoride of phosphorous in gaseous state was found to diffuse 2.12 times more slowly than nitrogen under similar conditions. Calculate the molecular mass and molecular formula of this fluoride which contains one atom of phosphorous per molecule.
- Q.6** The density of gas A is twice that of B at the same temperature the molecular weight of gas B is thrice that of A. The ratio of pressure of gas A and gas B will be –  
(A) 1 : 6 (B) 7 : 8  
(C) 6 : 1 (D) 1 : 4
- Q.7** Which one of the following is not correct about universal gas constant R ?  
(A) R = 0.0821 m<sup>3</sup> atm K<sup>-1</sup> mol<sup>-1</sup>  
(B) R = 8.341 kJ K<sup>-1</sup> mol<sup>-1</sup>  
(C) R = 1.987 k. cal °C<sup>-1</sup> mol<sup>-1</sup>  
(D) All of these
- Q.8** The partial pressure of a dry gas is –  
(A) Less than that of wet gas  
(B) Greater than that of wet gas  
(C) Equal to that of wet gas  
(D) None of these
- Q.9** Absolute zero is –  
(A) -273°C  
(B) Zero K  
(C) Temp. at which no substance exists in gaseous state.  
(D) All of these
- Q.10** The rate of diffusion of a gas is proportional to –  
(A) P / √d (B) P/d  
(C) √P / d (D) √P / d
- Q.11** A spherical air bubble is rising from the depth of a lake when pressure is P atm & temperature is TK. The percentage increase in its radius when it comes to the surface of lake will be (Assume temperature & pressure at the surface to be respectively 2TK & P/4)  
(A) 100% (B) 50%  
(C) 40% (D) 200%

**Q.12** Calculate the molar mass of a gas whose density at 27°C and 760mm pressure is 3.43 gL<sup>-1</sup>.

**ANSWERS**

- (1) 475.12 cm<sup>3</sup> (2) (C) (3) 2.03 × 10<sup>-2</sup> mol  
(4) 516.6 mm Hg (5) 126, PF<sub>5</sub> (6) (C)  
(7) (D) (8) (A) (9) (D)  
(10) (A) (11) (A) (12) 84.48

**KINETIC THEORY OF GASES**

- \* It was commonly given for ideal gases.
- \* This theory was proposed by Bernoulli and next developed by Clausius, Maxwell, Kroning and Boltzman.

**Assumptions of Kinetic theory of gases :**

- \* All the gases are made up of molecules moving randomly in all the direction.
- \* The volume of the individual molecule is negligible as compared to the total volume of the gas.
- \* Pressure exerted by gas is due to collision of gas molecules with the wall of the container so, Pressure ∝ No of collisions per unit time per unit area by the molecules on the wall of the container.
- \* All collisions between two molecules or between a molecule and a wall are perfectly elastic.
- \* All the molecules obey Newton's law of motion.
- \* Gas molecules neither attract nor repel each other.
- \* Kinetic energy of gas molecules depend upon the absolute temperature so, Kinetic energy ∝ absolute temperature
- \* The force of gravity has no effect on the speed of gas molecules.

**Calculation of Kinetic energy :**

According to postulates of kinetic gas equation

$$PV = \frac{1}{3} mn\bar{v}^2, \text{ where, } P = \text{pressure of the gas,}$$

V = volume of the gas

n = no of molecules present in the given amount of gas

$\bar{v}$  = Root mean square speed.

For one mole of the gas :

$$PV = RT \text{ and } n = N$$

$$\frac{1}{3} mN\bar{v}^2 = RT$$

$$\text{or } \frac{2}{3} \cdot \frac{1}{2} mN\bar{v}^2 = RT$$

$$\left( \therefore \frac{1}{2} mN\bar{v}^2 = \text{K.E. per mole} \right) \therefore \frac{2}{3} \text{K.E.} = RT$$

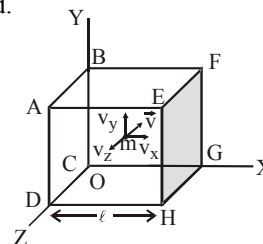
$$\text{K.E. per mole / Avg. K.E. per mole. ; } \text{K.E.} = \frac{3RT}{2}$$

∴ Boltzmann constant

$$k = R/N = 1.38 \times 10^{-16} \text{ ergs K}^{-1} \text{ molecules}^{-1}$$

⇒ K.E. per molecule / Avg K.E. per molecule

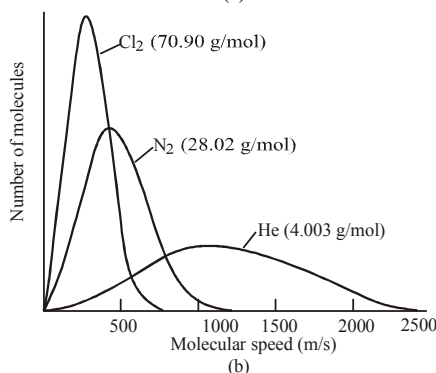
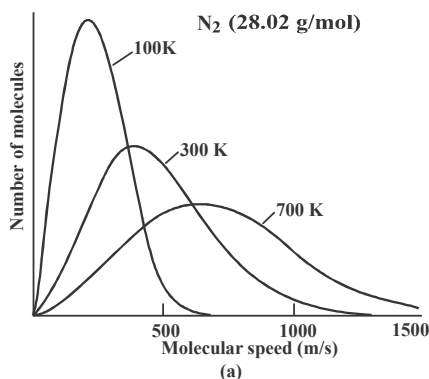
$$\text{K.E.} = \frac{3kT}{2}$$





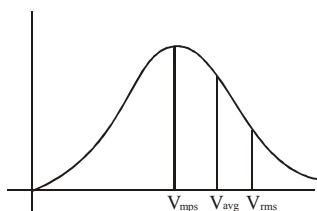
**Maxwell speed distribution curves :**

- \* Figure (a) shows typical Maxwell speed distribution curves for nitrogen gas at three different temperatures. At a given temperature, the distribution curve tells us the number of molecules moving at a certain speed. The peak of each curve represents the **most probable speed**, that is, the speed of the largest number of molecules.



**Figure :** (a) The speed distribution of speeds for nitrogen gas at three different temperatures. At the higher temperatures, more molecules are moving at faster speeds. (b) The distribution of speeds for three gases at 300 K. At a given temperature, the lighter molecules are moving faster, on the average.

- \* Note that the most probable speed increases as temperature increases (the peak shifts toward the right). Furthermore, the curve also begins to flatten out with increasing temperature, indicating that larger numbers of molecules are moving at greater speed.
- Figure (b) shows the speed distributions of three gases at the same temperature. The difference in the curves can be explained by noting that lighter molecules move faster, on average, than heavier ones.
- \* Representation of  $V_{mps}$ ,  $V_{avg}$  and  $V_{rms}$  on a curve plotted between fraction of molecules versus speed

**Speed related to gaseous state**

- (a) **Root mean square speed (RMS speed) :** Square root of the mean of the squares of the speed of all the molecules,

$$C = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$$

- (b) **Average speed :** It is the arithmetic mean of the various speeds of the molecules. Average speed =  $\sqrt{\frac{8RT}{\pi M}}$

$$\text{Average speed} = 0.9213 \times \text{RMS speed}$$

$$\text{RMS speed} = 1.085 \times \text{Average speed}$$

- (c) **Most probable speed :** Speed possessed by maximum number of molecules of a gas at a given temperature.

$$\text{Most probable speed} = \sqrt{\frac{2RT}{M}}$$

$$\text{MPS} = .816 \times \text{RMS} ; \text{RMS} = 1.224 \text{ MPS}$$

$$\text{MPS} : \text{A.V. speed} : \text{RMS} = 1 : 1.128 : 1.224$$

**MEAN FREE PATH ( $\lambda$ )**

- \* The distance travelled by the gaseous molecule between the two successive collision is known as mean free path

$$\text{which is denoted by } \lambda (\lambda) = \frac{1}{\sqrt{2} \pi \sigma^2} \cdot \frac{RT}{PV}$$

- \* As size of gas molecules increases mean free path decreases.
- \* At the room temperature and at the pressure of 1 atm, the order of mean free path is of  $10^{-5}$  cm.

**COLLISION FREQUENCY**

- \* The total number of collisions occurring in a unit volume of a gas per second under given set of conditions.

$$z \propto T^{2/3} \quad (\text{at constant } P)$$

$$z \propto P^2 \quad (\text{at constant } T)$$

- \* The total number of bimolecular collision per unit time is

$$\text{given by : } \frac{1}{\sqrt{2}} \pi \sigma^2 U_{avg} N^*2$$

where  $\sigma$  is the average diameter of two molecules,  
 $N^*$  is no. of molecules per unit volume

**Example 10 :**

Average speed of  $\text{CO}_2$  at the temperature  $T_1$  K and maximum possible velocity of  $\text{CO}_2$  at the temperature  $T_2$  K is  $9 \times 10^{-4}$  cm second $^{-1}$  then calculate value of  $T_1$  and  $T_2$ .

**Sol.** Average speed =  $\sqrt{\frac{8RT}{\pi M}}$  ; max. possible speed =  $\sqrt{\frac{2RT}{M}}$

$$\text{Average speed} = \text{Maximum possible velocity} \\ = 9 \times 10^4 \text{ cm sec}^{-1} = 9 \times 10^2 \text{ meter/ second}$$

$$9 \times 10^2 = \sqrt{\frac{8 \times 8.314 \times T_1}{3.14 \times 44 \times 10^{-3}}} ; 9 \times 10^2 = \sqrt{\frac{2 \times 8.314 \times T_2}{44 \times 10^{-3}}}$$

$$\text{On solving } T_1 = 1682.5 \text{ K, } T_2 = 2143.4 \text{ K}$$

**DEGREE OR FREEDOM (f):**

The term degree of freedom refers to the number of possible independent ways in which a system can have energy.

**Degree of freedom of gas molecules**

A gas molecule can have following types of energies :

- (i) Translational K.E.                      (ii) Rotational K.E.  
 (iii) Vibrational energy (potential + kinetic)

**Degree of freedom (f) in different gas molecules**

Molecules	Translational	Rotational
Monatomic	3	0
Diatomic	3	2
Polyatomic	3	2 (linear molecule) 3 (non-linear molecule)

**MAXWELL'S LAW OF EQUIPARTITION OF ENERGY**

For a dynamical system in thermal equilibrium, the energy of the system is equally distributed amongst the various degrees of freedom and the energy associated with each

degree of freedom per molecule is  $\frac{1}{2}kT$

Translational kinetic energy of a molecule,  $\frac{1}{2}mv_{rms}^2 = \frac{3}{2}kT$

we have  $\frac{1}{2}mv_{rmsx}^2 + \frac{1}{2}mv_{rmsy}^2 + \frac{1}{2}mv_{rmsz}^2 = \frac{3}{2}kT$

**SPECIFIC HEAT OF GASES**

(a) **Specific Heat** - It is the amount of heat required to raise the temperature of one gm of the substance through one degree centigrade. It is usually expressed in "Calories".

(b) **Calorie** - A calorie is defined as the amount of heat required to raise the temperature of one gm of water through 1°C (more accurately from 15.5°C to 16.5°C).

The heat so supplied is used up in increasing the internal energy of the molecule, i.e. in raising the temperature or in raising the average K.E. of the molecules.

(c) **Specific Heat of a gas at constant volume ( $C_V$ ):**

The amount of heat required to raise the temperature of one gm of the gas by 1°C when the volume is kept constant and pressure is allowed to increase.

(d) **Specific Heat of gas at constant Pressure ( $C_p$ ):**

The amount of heat required to raise the temperature of one gm of the gas 1°C when the pressure is kept constant and volume is allowed to increase.

$$C_V = c_V \times M \quad \text{and} \quad C_p = c_p \times M$$

Where  $C_V$  and  $C_p$  are molar specific heat or heat capacity per mole at constant volume and constant pressure.

(e) **Ratio for Molar Heats -**

(i) For monoatomic gases  $\frac{C_p}{C_V} = \gamma = \frac{5.0}{3.0} = 1.66$

∴ Molar heat capacity at constant volume

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

$$\text{At } 1^\circ\text{C} \Rightarrow K.E. = \frac{3}{2}R; K.E. = \frac{3}{2} \times 2 = 3$$

Therefore,  $C_V = 3$  calories.

$$\& C_p = \text{Increase in K.E.} \left( \frac{3}{2}R \right) + \text{work done } P \Delta V$$

$$= \frac{3}{2}R + R = \frac{5}{2}R \text{ (Since } R = 2); C_p = \frac{5}{2} \times 2 = 5 \text{ calories.}$$

(ii) For diatomic gases  $\frac{C_p}{C_V} = \frac{5+x}{3+x}$

In case of diatomic gases x in many cases is 2.

$$\frac{C_p}{C_V} = \frac{7}{5} = 1.40$$

(iii) For triatomic gases  $\frac{C_p}{C_V} = \frac{5+3}{3+3} = \frac{8}{6} = 1.33$

**Example 11 :**

Find the number of degrees of freedom of molecules in a gas whose molar heat capacity at constant pressure is 29 J/mole.K. [R = 8.31 J/mole.K]

**Sol.**  $C_p = 29$  J/mole.K,  $C_V = C_p - R = 29 - 8.31 = 20.69$

$$\gamma = \frac{C_p}{C_V} = \frac{29}{20.69} = 1.40; \gamma = \frac{2}{f} + 1; \frac{2}{f} + 1 = 1.4; f = \frac{2}{0.4} = 5$$

**TRY IT YOURSELF-2**

- Q.1** Calculate RMS velocity of oxygen if 6.431 g of it occupies 5L at 750mm.
- Q.2** Calculate the temperature at which  $\text{CO}_2$  has the same RMS velocity as that of  $\text{O}_2$  at STP.
- Q.3** Which of the following postulate of kinetic theory of gas is responsible for deviation from ideal behaviour?  
 (A) Kinetic energy of the gas molecules increases with increase in temperature.  
 (B) Collisions among the gas molecules are perfectly elastic.  
 (C) There is no forces of attraction or repulsion among gas molecules.  
 (D) Molecules in a gas follow zig-zag path.
- Q.4** If pressure of a gas increases upto nine times keeping temperature constant, then its rms velocity will become –  
 (A) 9 times                                      (B) 3 times  
 (C) remains same                              (D) 1/3 time
- Q.5** Pressure exerted by one mole of an ideal gas kept in vessel of V, L having root mean square speed of molecules v and m mass of each molecule is correctly given by the equation

$$(A) P = \frac{1}{2} \frac{N_A}{V} mv^2$$

$$(B) P = \frac{1}{3} \frac{N_A}{V} mv^2$$

$$(C) P = \frac{2}{3} \frac{N_A}{V} mv^2$$

$$(D) P = \frac{3}{2} \frac{N_A}{V} mv^2$$

- Q.6** The ratio between the rms velocity of  $H_2$  at 50K and that of  $O_2$  at 800 K is –  
 (A) 4 (B) 2  
 (C) 1 (D) 1/4
- Q.7** At what temperature will most probable speed of the molecules of second member of homologous series  $C_nH_{2n-2}$  be same as that of Bromine gas at  $527^\circ C$   
 (A)  $200^\circ C$  (B)  $-73^\circ C$   
 (C)  $+73^\circ C$  (D)  $-200^\circ C$
- Q.8**  $U_{rms}$  of ideal gas A at T K is equal to  $U_{mp}$  of another ideal gas B at  $(T/2)$  K. The ratio of their molecular masses,  $M_A : M_B$  is –  
 (A) 1 : 2 (B) 1 : 3  
 (C) 3 : 2 (D) 3 : 1
- Q.9** With regard to the gaseous state of matter which of the following statements are correct?  
 (A) Complete order of molecules  
 (B) Complete disorder of molecules  
 (C) Random motion of molecules  
 (D) Fixed position of molecules
- Q.10** For  $H_2$  gas  $C_p - C_v = a$  and for  $O_2$  gas  $C_p - C_v = b$ , so the relation between a and b is –  
 (A)  $a = 16b$  (B)  $16a = b$   
 (C)  $a = 4b$  (D)  $a = b$
- Q.11** Value of  $\gamma$  for  $CH_4$  molecule is –  
 (Consider vibrational degree of freedom to be active)  
 (A) 4/3 (B) 13/12  
 (C) 15/14 (D) 17/15

**ANSWERS**

- (1)  $4.83 \times 10^4 \text{ cm s}^{-1}$  (2) 375.38 K (3) (C)  
 (4) (C) (5) (B) (6) (C)  
 (7) (B) (8) (D) (9) (BC)  
 (10) (D) (11) (B)

**Example 12 :**

The compressibility factor for 1 mole of a van der Waals gas at  $0^\circ C$  and 100 atm pressure is found to be 0.5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant, a.

**Sol.** For 1 mole of the gas,

$$Z = \frac{pV}{RT} \Rightarrow 0.5 = \frac{100 \times V}{0.0821 \times 273}; V = 0.112 \text{ L}$$

Neglecting b, van der Waals equation reduces to

$$\left(P + \frac{a}{V^2}\right)V = RT \quad \text{or} \quad pV + \frac{a}{V} = RT$$

$$\text{or} \quad 100 \times 0.112 + \frac{a}{0.112} = 0.0821 \times 273$$

$$a = 1.25 \text{ L}^2 \text{ atm mol}^{-2}.$$

**DEVIATIONS FROM IDEAL BEHAVIOUR**

- \* An ideal gas is one which obeys the gas laws of the gas equation  $PV = nRT$  at all pressure and temperatures. However no gas in nature is ideal.
- \* Almost all gases show significant deviations from the ideal

behaviour. Thus the gases  $H_2$ ,  $N_2$  and  $CO_2$  which fail to obey the ideal-gas equation are termed as non-ideal or real gases.

**Causes of deviation from ideal behaviour :**

The following two assumptions of the kinetic theory of gases are faulty

- (a) The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.
- (b) The forces of attraction or repulsion between the gas molecules are negligible.

The above assumptions are correct only if the temperature is high or pressure is low.

- \* In a plot  $pV$  vs  $p$  for gases at constant temperature,  $pV$  will be constant (Boyle's law) and  $pV$  vs  $p$  graph at all pressures will be a straight line parallel to x-axis. Fig. shows such a plot constructed from actual data for several gases at 273K.
- \* At constant temperature  $pV$  vs  $p$  plot for real gases is not a straight line.
- \* For dihydrogen and helium, as the pressure increases the value of  $pV$  also increases.
- \* For carbon monoxide and methane, first there is a negative deviation from ideal behaviour, the  $pV$  value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that  $pV$  value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously.

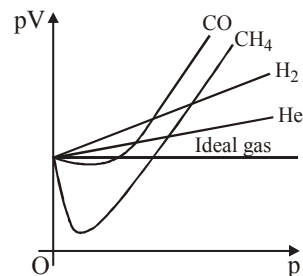


Figure : Plot of  $pV$  vs  $p$  for real gas and ideal gas

- \* The pressure vs volume plot of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide. Figure shows these plots.
- \* It is apparent that at very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.

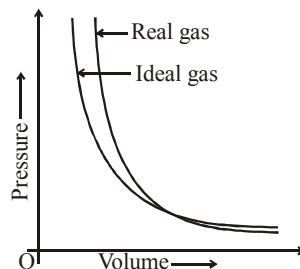


Fig : Plot of pressure vs volume for real gas and ideal gas

\* **Compressibility Factor** : The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the compressibility factor, denoted

$$\text{by } Z. \text{ It is defined as } Z = \frac{PV}{nRT}; Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

\* The deviations from ideality may be shown by a plot of the compressibility factor  $Z$ , against  $P$ .

\* For an ideal gas,  $Z = 1$  and it is independent of temperature and pressure.

\* The deviations from ideal behaviour of a real gas will be determined by the value of  $Z$  being greater or less than 1.

\* The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called **Boyle temperature or Boyle point**.

\* Above their Boyle point, real gases show positive deviations from ideality and  $Z$  values are greater than one.

\* Below Boyle temperature real gases first show decrease in  $Z$  value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of  $Z$  increases continuously.

\* The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of non ideality of the gas.

\* For a real gas, the deviations from ideal behaviour depends on: (i) pressure ; (ii) temperature.

This can be illustrated by examining the compressibility curves of some gases.

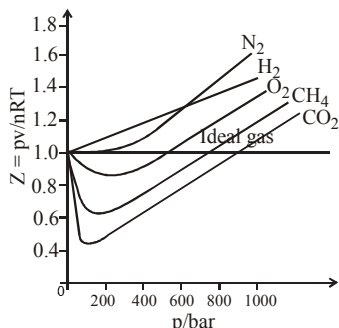


Figure : Effect of pressure variation on deviations

From the above curves we can conclude that:

- At low pressure and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.
- At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.
- Greater is the departure of  $Z$  from unity, more is the deviation from ideal behaviour.
  - When  $Z < 1$ , this implies that gas is more compressible.
  - When  $Z > 1$ , this means that gas is less compressible.
  - When  $Z = 1$ , the gas is ideal.

### VANDER WALL'S EQUATION

\* Real gases show deviations from ideal gas law because molecules interact with each other.

At high pressures molecules of gases are very close to each other. Molecular interactions start operating.

\* At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container.

\* **Pressure correction** : The pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$P_{\text{ideal}} = \underset{\substack{\text{observed} \\ \text{pressure}}}{P_{\text{real}}} + \underset{\substack{\text{correction} \\ \text{term}}}{\frac{an^2}{V^2}}$$

\* **Volume Correction** : The observed volume is greater than ideal volume & correction term 'nb' has to be subtracted from observed volume in order to get ideal volume.

$$V_{\text{ideal}} = V - nb$$

$$\text{For } n \text{ mole, } \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

where 'a' is the constant of proportionality which depends on the nature of gas. Higher value of 'a' reflects the increased attraction between gas molecules.

\* The Vander Waals constant b (the excluded volume) is actually 4 times the volume of a single molecule. i.e.  $b = 4 \cdot \frac{1}{3} N_A V$ , where  $N_A \rightarrow$  Avogadro number.

$$\therefore b = 4 \times 6.023 \times 10^{23} \times \frac{4}{3} \pi r^3,$$

where  $r$  is the radius of a molecule.

\* **The constant a and b**: Vander Waals constant for attraction (a) and volume (b) are characteristic for a given gas. Some salient features of 'a' and 'b' are:

- For a given gas Vander Waal's constant of attraction 'a' is always greater than Vander Waals constant of volume (b).
- The gas having higher value of 'a' can be liquified easily and therefore  $H_2$  and He are not liquified easily.
- The numerical values of a and b are in the order of  $10^{-1}$  to  $10^{-2}$  to  $10^{-4}$  respectively.
- 'a' factor depends on inter-molecular attractive forces. 'a' factor for polar molecule > 'a' factor for non-polar molecule.
- A high value of 'a' suggests that vander Waals forces in these gases are strong. The larger the value of 'b', the larger the molecular volume and diameter. For example,  $SO_2$  gas has a larger molecular volume and molecular diameter than  $H_2O$  vapours because 'b' for  $SO_2$  (0.0564) is greater than for  $H_2O$  (0.0305).
- The values of 'a' and 'b' for some gases are given below:

Gas	He	$H_2$	$O_2$	$N_2$	$CH_4$
a	0.034	0.244	1.360	1.390	2.253
b	0.0237	0.0266	0.318	0.0391	0.0428
Gas	$CO_2$	$H_2O$	$C_2H_6$	$SO_2$	
a	3.592	5.462	5.489	6.714	
b	0.0427	0.0305	0.0638	0.0564	

These values clearly indicate, why gases such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_6$  and  $\text{SO}_2$  show large deviations from ideal behaviour.

**Note :**

- \* At low pressure and very high temperature :  $V_m$  will be very large, hence  $b$  can be neglected and  $a/V_m^2$  can also be neglected as  $V_m$  is very large.  
 $PV_m = RT$  (ideal gas condition)
- \* For  $\text{H}_2$  or He at  $a \approx 0$  because molecules are smaller in size or vander Wall's forces will be very weak, these are non polar so no dipole-dipole interactions are present in the actions.  $P(V_m - b) = RT$ , so  $Z = 1 + \frac{Pb}{RT}$

**Limitations of van der Waal's gas equation**

- \* It could not explain the quantitative aspect of deviation satisfactorily as it could explain the qualitative aspect of deviations.
- \* The values of 'a' & 'b' were also found to vary with P & T.

**Virial Equation of state for 1 Mole of gas :**

$$Z = \frac{PV}{RT} = 1 + B\frac{1}{V} + C\frac{1}{V^2} + D\frac{1}{V^3} + \dots$$

$B$  = second virial co-efficient ,

temperature dependent =  $b - \frac{a}{RT}$ ,  $C$  = third virial coefficient,

temperature dependent =  $b^2$

**TIPS**

- \* The difference between most probable speed of molecules of gas, root mean square speed and average speed decreases as the temperature is increased.
- \* Average speed =  $0.9213 \times \text{R.M.S. speed}$ .
- \* Most probable speed =  $\sqrt{2/3} \times \text{Root mean square speed}$ .
- \* R.M.S. Velocity =  $1.085 \times \text{Average speed}$ .
- \* Most probable speed =  $0.8166 \times \text{R.M.S. speed}$ .
- \* For a vander Waals fluid,  $a/b$  has the dimension of energy per mole
- \* The vander Waals constant  $a$  for He, Ne,  $\text{H}_2$  and  $\text{N}_2$  are 0.0341, 0.2107, 0.244 and 1.39 litre<sup>2</sup>- atom/mole<sup>2</sup> respectively. This indicates that He is most difficult to be liquefied among above gases. Out of  $\text{C}_2\text{H}_4$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$  vapour,  $\text{C}_2\text{H}_4$  can be easily liquefied.
- \* The vander Waals constant  $a$  generally increases with increase in the boiling point of the gas, because high boiling point implies strong intermolecular attractive forces.

**LIQUIFACATION OF GASES**

- \* The conversion of gases into liquid is called as liquefaction of gases. During liquefaction intermolecular force of attraction increases.
- \* The gas can be liquefied by increasing pressure or by cooling or by combined effect of both.
- \* Both factors increases intermolecular force of attraction and decreases kinetic energy of gaseous molecules.

\* The gases such as  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  etc. can be liquefied by increasing pressure at room temperature or by cooling. But the gases such as  $\text{H}_2$ , He,  $\text{O}_2$  and  $\text{N}_2$  etc. could not be liquefied by increasing pressure at room temperature and named as permanent gases.

\* Gases which deviate more from their ideal behaviour can be liquefied easily.

\* **Joule-Thomson effect:** It states that if a real gas expands adiabatically under high pressure through a fine orifice into a region of low pressure results in cooling of gas.

\* **Inversion Temperature ( $T_i$ ) :**

The temperature at which there is no heating or cooling of gas occur during adiabatic expansion based on Joule Thomson effect. But the temperature below inversion temperature results in cooling of gas and above inversion temperature results in heating of gas.

$$T_i = \frac{2a}{bR}$$

$T_i$  = Inversion temperature

$a$  &  $b$  = van der Waal's constant,  $R$  = Gas constant

\* **Boyle's temperature ( $T_b$ ) or Boyle's point :**

The temperature at which real gases behave like ideal gases for a long range of pressure.

$$T_b = \frac{a}{bR} ; T_b = \frac{T_i}{2} \text{ or } T_i = 2T_b$$

**Behaviour of Carbondioxide near liquefaction temperature :**

T. Andrews studied the behaviour of carbon dioxide in the neighbourhood of its liquefaction temperature.

He observed that –

- \* Above  $48^\circ\text{C}$ , all isotherms are smooth hyperbolic similar to that expected for an ideal gas.
- \* At temperatures above  $31.01^\circ\text{C}$ , but below  $48^\circ\text{C}$  the pressure-volume isotherms are badly distorted, indicating a significant departure from the ideal gas behaviour.
- \* At  $31.01^\circ\text{C}$ , an increase in pressure from ordinary pressure (along the curve ab) causes a decrease in the volume until at 72.85 atm pressure (point b), where liquid  $\text{CO}_2$  appears. Further increase in pressure does not cause much change in the volume because liquids are very much less compressible.

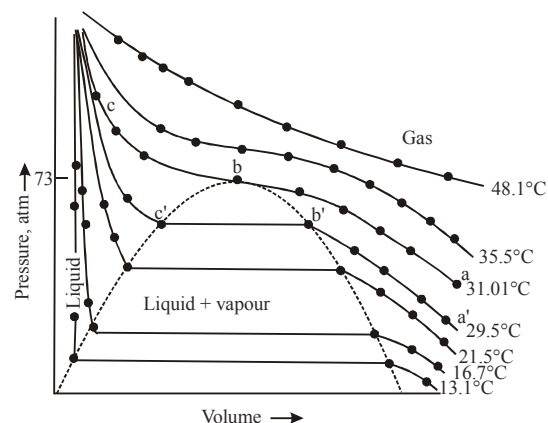


Figure : Isotherms of  $\text{CO}_2$  at various temperature

- \* Below 31.01°C (say at 29.5°C), the isotherm shows gaseous character at low pressures, (from a' to b'), but shows a sudden discontinuity when the pressure is increased. The gas shows signs of condensation, and suffers an appreciable change in the volume, even when the pressure remains virtually unchanged. After the condensation is complete (at c'), the change in volume with an increase in pressure is very small.
- \* Similar isotherms are obtained at still lower temperatures except that the horizontal portion of the isotherm goes on increasing. The extremes of these horizontal lines lie on a smooth curve. This curve is called the co-existence curve. Outside this curve either only the gas (on the right of the curve) or only the liquid (on the left of the curve) exists. Inside the dome-shaped curve, the liquid and the vapour exist in equilibrium.

**Critical temperature ( $T_c$ )** : It is defined as the characteristic temperature for a given gas below which a continuous increase in pressure will bring liquification of gas and above which no liquefaction is noticed although pressure may be increased. e.g.  $T_c$  for  $\text{CO}_2$  is 31.2°C.

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

**Critical pressure ( $P_c$ )** : It is defined as the minimum pressure applied on 1 mole of gas placed at critical temperature, to just liquefy the gas.

For  $\text{CO}_2$ ,  $P_c = 73.87 \text{ bar}$        $P_c = \frac{a}{27b^2}$

**Critical Volume ( $V_c$ )** : The volume occupied by 1 mole of gas at critical temperature and pressure.  $V_c = 95 \times 10^{-6} \text{ m}^3$ .

$$V_c = 3b$$

### TIPS

- \* Substances in which molecular forces of attraction are large (e.g. polar molecules such as  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{NH}_3$  etc) have high critical temperatures than those in which intermolecular forces of attraction are small (e.g.  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , Ar etc.)
- \* At critical temperature the distinction between gaseous state and liquid state disappears and there is an equilibrium between gaseous state and liquid state (both forms co-exist).
- \* At critical temperature both intermolecular as well as interatomic attractions are high.
- \* Critical temperature for water,  $\text{CO}_2$ ,  $\text{O}_2$  and  $\text{H}_2$  are 370°C, 31.1°C, -118.8°C and -240°C respectively.
- \* Favourable conditions for liquefaction of gases are low temperatures and high pressures.
- \* Gases like  $\text{O}_2$ ,  $\text{N}_2$  etc. cannot be liquefied at room temperature by applying pressure, because of their low critical temperatures.

### TRY IT YOURSELF-3

- Q.1** The value of van der Waal's constant 'a' for gases  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$  and  $\text{CH}_4$  are x, y, z and c respectively, where  $z > c > y > x$ . The gas which can most easily be liquified, is  
(A)  $\text{O}_2$  (B)  $\text{N}_2$  (C)  $\text{NH}_3$  (D)  $\text{CH}_4$

- Q.2** Which of the following is correct ?  
(A) A real gas approaches ideal gas behaviour at low pressure and high temperature.  
(B) Liquification of a real gas is possible at low temperature and high pressure.  
(C) Both of them (D) None of them
- Q.3** Which of the following option correctly represent the values of Van der Waal's constant a for gases  $\text{H}_2$ ,  $\text{O}_2$  and  $\text{N}_2$  in  $\text{atm-lit}^2/\text{mol}^2$ ?  
(A) 4, 3.2, 1.6 (B) 3.2, 1.6, 4 (C) 1.6, 4, 3.2 (D) 1.6, 3.2, 4
- Q.4** 30gms of oxygen gas present in a volume of 20L at a pressure of 1atm and temperature of 273 K. Comment on the nature of the dominant force.  
(A) Attractive  
(B) Repulsive  
(C) Neither attractive non repulsive  
(D) Both attractive and repulsive
- Q.5** Gases possess characteristic critical temperature which depends upon the magnitude of intermolecular forces between the particles. Following are the critical temperatures of some gases.
- | Gases                    | $\text{H}_2$ | He  | $\text{O}_2$ | $\text{N}_2$ |
|--------------------------|--------------|-----|--------------|--------------|
| Critical temp. in Kelvin | 33.2         | 5.3 | 154.3        | 126          |
- From the above data what would be the order of liquefaction of these gases? Start writing the order from the gas liquefying first  
(A)  $\text{H}_2$ , He,  $\text{O}_2$ ,  $\text{N}_2$  (B) He,  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$   
(C)  $\text{N}_2$ ,  $\text{O}_2$ , He,  $\text{H}_2$  (D)  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{H}_2$ , He
- Q.6** Under which of the following two conditions applied together, a gas deviates most from the ideal behaviour?  
(A) Low pressure (B) High pressure  
(C) Low temperature (D) High temperature
- Q.7** Positive deviation from ideal behaviour takes place because of –  
(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  $\frac{PV}{nRT} < 1$
- Q.8** A gas described by van der Waal's equation –  
(A) behaves similar to an ideal gas in the limit of large molar volumes.  
(B) behaves similar to an ideal gas in the limit of large pressures.  
(C) is characterized by van der Waal's coefficients that are dependent on the identify of the gas but are independent of the temperature.  
(D) has the pressure that is lower than the pressure exerted by the same gas behaving ideally.

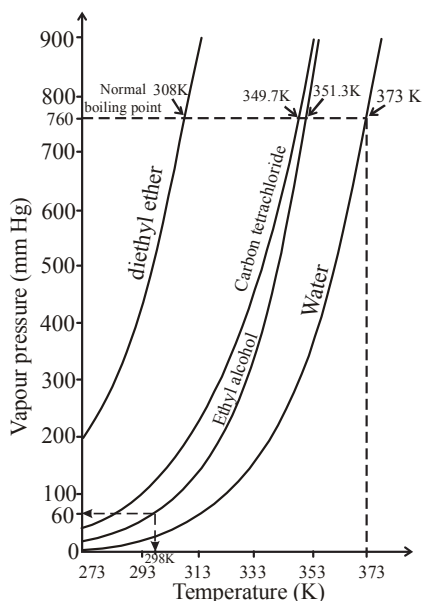
### ANSWERS

- (1) (C)                      (2) (C)                      (3) (C)  
(4) (A)                      (5) (D)                      (6) (BC)  
(7) (C)                      (8) (ACD)

## LIQUID STATE

### 1. Vapour pressure :

- \* The pressure of the vapour present at equilibrium (Rate of condensation = Rate of evaporation) is called the equilibrium vapour pressure, or more commonly, the **vapour pressure** of the liquid.
- \* At **boiling point**, the vapour pressure of a liquid becomes equal to the atmospheric pressure. Thus, the boiling point of a liquid depends upon the pressure over the surface of the liquid.
- \* The temperature at which the vapour pressure becomes equal to 1 atm is called the **normal boiling point**.
- \* If pressure is 1 bar then the boiling point is called **standard boiling point** of the liquid.
- \* Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure.
- \* The normal boiling point of water is 100°C (373K), its standard boiling point is 99.6°C (372.6K).
- \* Liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food.
- \* In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.
- \* When density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called **critical temperature**.
- \* Vapour pressure of some common liquids at various temperatures is given in figure.



**Figure : Vapour pressure vs temperature curve of some common liquids.**

### 2. Surface tension :

- \* The resistance of a liquid to an increase in its surface area is called the surface tension of the liquid.
- \* The energy required to increase the surface area of the liquid by one unit is defined as surface energy.
- \* Surface tension is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid.
- \* Liquid tends to rise (or fall) in the capillary because of surface tension. Liquids wet the things because they spread across their surfaces as thin film.
- \* Moist soil grains are pulled together because surface area of thin film of water is reduced. It is surface tension which gives stretching property to the surface of a liquid.
- \* On flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.
- \* Increase in pressure on the surface of a liquid increases the surface tension. Such effects are, however, not very large.
- \* Impurities affect surface tension appreciably. It is observed that the impurities which tend to concentrate in the surface of the liquid as compared to the bulk, lower the surface tension. Substances like alcohols, soaps, detergents, etc., lower the surface tension of water. Inorganic impurities, e.g., NaCl etc., tend to increase the surface tension of water.
- \* Surface tension decreases with increase in temperature because with the increase in temperature, kinetic energy of molecules increases. As a result, intermolecular forces decreases & hence force acting per unit length decreases.

### 3. Viscosity :

- \* The property of a fluid by virtue of which it oppose the relative motion between its different layers is known as viscosity and the force that is into play is called the viscous force.
- \* According to Newton, the viscous force acting tangentially to the layer is proportional to the area of the layer and the speed gradient at the layer. If  $F$  is the viscous force on the layer, then  $F \propto A$ , where  $A$  is the area of the layer. Also,

$$F \propto -\frac{dv}{dx} \Rightarrow F = -\eta A \frac{dv}{dx} \quad (\text{The negative sign is put to}$$

account for the fact that the viscous force is opposite to the direction of motion.)

where  $\eta$  is a constant depending upon the nature of the liquid and is called the coefficient of viscosity.

- \* SI unit of viscosity coefficient is 1 newton sec. per square metre ( $\text{N s m}^{-2}$ ) = pascal second ( $\text{Pa s} = 1 \text{ kg m}^{-1} \text{ s}^{-1}$ ).
- \* In cgs system the unit of coefficient of viscosity is poise.  
1 poise =  $1 \text{ g cm}^{-1} \text{ s}^{-1} = 10^{-1} \text{ kg m}^{-1} \text{ s}^{-1}$
- \* Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity.
- \* Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids. However, property of flow of glass can be experienced by measuring the thickness of windowpanes of old buildings. These become thicker at the bottom than at the top.
- \* Viscosity of liquids decreases as the temperature rises.

**TRY IT YOURSELF-4**

- Q.1** If pressure is 1 bar, then the boiling temperature is called—  
(A) Normal boiling point (B) Standard boiling point  
(C) Abnormal boiling point (D) Simple boiling point
- Q.2** Choose the correct statement(s)  
(A) Boiling does not occur when liquid is heated in a closed vessel.  
(B) On heating continuously vapour pressure of a liquid increases in a closed vessel.  
(C) Liquids may be considered as a continuation of gas phase into a region of small volume and very strong molecular attractions.  
(D) All of these
- Q.3** Liquids tend to rise or fall in capillary because of—  
(A) Boiling (B) Evaporation  
(C) Surface tension (D) Viscosity
- Q.4** As the temperature rises viscosity of liquids —  
(A) Increases (B) Decreases  
(C) Remains same  
(D) Increases or decreases depending on the nature of liquid.
- Q.5** Which of the following property of water can be used to explain the spherical shape of rain droplets?  
(A) viscosity (B) surface tension  
(C) critical phenomena (D) pressure
- Q.6** What is SI unit of viscosity coefficient ( $\eta$ )?  
(A) Pascal (B)  $\text{Nsm}^{-2}$   
(C)  $\text{km}^{-2} \text{s}$  (D)  $\text{N m}^{-2}$
- Q.7** Increase in kinetic energy can overcome intermolecular forces of attraction. How will the viscosity of liquid be affected by the increase in temperature?  
(A) Increase (B) No effect  
(C) Decrease (D) None of these
- Q.8** How does the surface tension of a liquid vary with increase in temperature?  
(A) Remains same (B) Decreases  
(C) Increases (D) None of these

**ANSWERS**

- (1) (B) (2) (D) (3) (C)  
(4) (B) (5) (B) (6) (B)  
(7) (C) (8) (B)

**IMPORTANT POINTS**

- \* The energy of translation of a mole of gas is directly proportional to temperature and has the same value ( $3RT/2$ ) for all gases. The product of PV is a unit of energy.
- \* Pressure of dry gas = Total pressure – Aqueous tension.
- \* Rate of diffusion of a gas is directly proportional to its pressure because number of molecules per unit volume increases with pressure.
- \* The fluids above critical temperature are called as super critical fluids these are used to separate mixtures containing different component Such as  $\text{CO}_2$  is used to remove caffeine from coffee beans in place of chlorofluorocarbons.
- \* Ideal gas equation :  $PV = nRT$   
(i)  $R = 0.0821 \text{ liter atm. deg}^{-1} \text{ mole}^{-1}$

- (ii)  $R = 2 \text{ cal. deg}^{-1} \text{ mole}^{-1}$   
(iii)  $R = 8.314 \text{ JK}^{-1} \text{ mole}^{-1}$

\*  $\text{RMS speed } v = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{d}}$

Average speed =  $\sqrt{\frac{8RT}{M}}$

Most probable speed =  $\sqrt{\frac{2RT}{M}}$

MPS : A.V. speed : RMS = 1 : 1.128 : 1.224

\* Kinetic energy =  $\frac{3}{2} nRT$

\* Rate of diffusion  $\propto \frac{1}{\sqrt{\text{density of gas}}}$

\* Van der Waal's equation :  $\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$

\* The greater the value of 'a' greater is the ease with which a gas can be liquefied. For example, the values of a in the case of  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{Cl}_2$  and  $\text{SO}_2$  are 4.17, 3.59, 6.49 and 6.71 respectively. This shows that  $\text{SO}_2$  can be readily liquefied.

\* The gases with high molecular weight (when H-bonding is absent) can be easily liquefied.

\* Average speed is slightly higher than the most probable speed and R.M.S. speed is slightly higher than the average speed.

\*  $Z$  (compressibility factor) =  $\frac{PV}{nRT}$

$Z = 1$  for ideal gas

$Z > 1$  : +ve deviation,  $Z < 1$  : -ve deviation

**ADDITIONAL EXAMPLES**

**Example 1 :**

At fixed temperature and 600 mm pressure, the density of a gas is 42. At the same temperature and 700mm pressure, what is the density of the gas?

**Sol.** According to Boyle's law,  $P \propto \frac{1}{V}$  (at constant temperature)

Density  $D = \frac{\text{Mass (M)}}{\text{Volume (V)}}$  or  $D \propto \frac{1}{V}$  ;  $P \propto D$

$\frac{P_1}{D_1} = \frac{P_2}{D_2}$  ;  $D_2 = \frac{P_2 \times D_1}{P_1}$

$P_1 = 600, D_1 = 42, P_2 = 700$  ;  $D_2 = \frac{700 \times 42}{600} = 49$



**Example 2 :**

At what temperature, the volume of given amount of a gas at 25° C becomes twice, when pressure is kept constant?

**Sol.** According to Charles law,  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$  ;  $V_1 = v$   $V_2 = 2v$

$$T_1 = 273 + 25 = 298 \quad T_2 = ?$$

$$\frac{v}{298} = \frac{2v}{T_2} ; \quad T_2 = \frac{298 \times 2}{1} = 596 \text{ K}$$

**Example 3 :**

If pressure of a gas is reduced by 25%, then what should be the temperature required to make its volume twice at NTP?

**Sol.** According to combined gas equation,  $\frac{PV}{T} = \frac{P_1V_1}{T_1}$

$$P = 76.0, P_1 = 57.0 \text{ (on reducing by 25\%)}$$

$$V = 2v, V_1 = v, T = 273\text{K}, T_1 = ?$$

$$\frac{76 \times v}{273} = \frac{57 \times 2v}{T_1} ; \quad T_1 = \frac{273 \times 57 \times 2}{76} = 409.3 \text{ K}$$

**Example 4 :**

Total pressure of a gaseous mixture of 2.8 gram N<sub>2</sub>, 3.2 gram O<sub>2</sub> and 0.50 gram H<sub>2</sub> is 4.5 atmosphere, calculate the partial pressure of each gas.

**Sol.** Number of moles or =  $\frac{\text{Mass}}{\text{Molar mass}}$

$$n_{\text{N}_2} = \frac{2.8}{28} = 0.1 \text{ mole} ; \quad n_{\text{O}_2} = \frac{3.2}{32} = 0.1 \text{ mole}$$

$$n_{\text{H}_2} = \frac{0.5}{2} = 0.25 \text{ mole}$$

$$\text{Total number of mole} = 0.1 + 0.1 + 0.25 = 0.45$$

Partial pressure of a gas

$$= \frac{\text{No. of moles}}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$P_{\text{N}_2} = \frac{0.1}{0.45} \times 4.5 \text{ atm} = 1.0 \text{ atm} ;$$

$$P_{\text{O}_2} = \frac{0.1}{0.45} \times 4.5 \text{ atm} = 1.0 \text{ atm}$$

$$P_{\text{H}_2} = \frac{0.25}{0.45} \times 4.5 \text{ atm} = 2.5 \text{ atm}$$

**Example 5 :**

Under similar conditions, 160 ml hydrocarbon diffuses in 16 minutes and 150 ml of sulphur dioxide in 30 minutes. If molecular weight of sulphur dioxide is 64, then find out the molecular weight of hydrocarbon.

**Sol.** Hydrocarbon                      Sulphur dioxide  
 $V_1 = 160 \text{ ml}$                        $V_2 = 120 \text{ ml}$   
 $t_1 = 16 \text{ minute}$                        $t_2 = 20 \text{ minute}$   
 $M_1 = ?$                                        $M_2 = 64,$

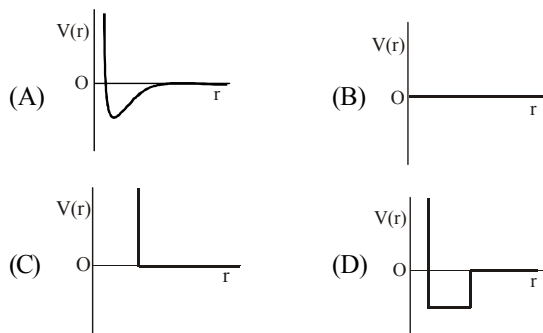
From Graham's law

$$\frac{V_1 / t_1}{V_2 / t_2} = \sqrt{\frac{M_2}{M_1}} ; \quad \frac{160 / 16}{150 / 30} = \sqrt{\frac{64}{M_1}}$$

$$2 = \sqrt{\frac{64}{M_1}} \quad M_1 = 4 = \frac{64}{M_1} = M_1 = \frac{64}{4} = 16$$

**Example 6 :**

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



**Sol.** (C).  $P(V - b) = RT$

$$\Rightarrow PV - Pb = RT \Rightarrow \frac{PV}{RT} = \frac{Pb}{RT} + 1 \Rightarrow Z = 1 + \frac{Pb}{RT}$$

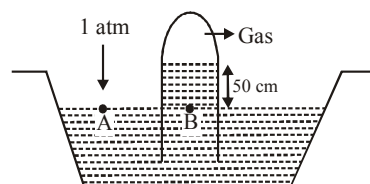
Hence  $Z > 1$  at all pressures.

This means, repulsive tendencies will be dominant when interatomic distance are small.

This means, interatomic potential is never negative but becomes positive at small interatomic distances.

**Example 7 :**

Calculate the pressure of the gas in the following arrangement:



**Sol.**  $P_A = P_B$

At the equilibrium position,  $P_{\text{atm}} = P_{\text{gas}} + P_{\text{Hg}}$   
 $76\text{cm} = P_{\text{gas}} + 50 ; \quad P_{\text{gas}} = 26\text{cm}.$

**Example 8 :**

A gas occupies a volume of 580 ml at 17°C. It is heated to 100°C at constant pressure. Calculate the volume of the gas.

**Sol.** Initial volume ( $V_1$ ) = 580 ml,

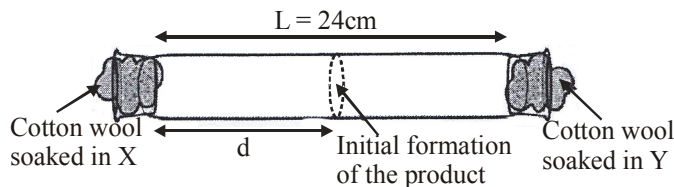
$$T_1 = 17 + 273 = 290 \text{ K}, \text{ Final volume } (V_2) = ?$$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \therefore V_2 = T_2 \times \frac{V_1}{T_1} = 373 \times \frac{580}{290} = 746 \text{ ml}.$$

**For Example 9 & 10**

X and Y are two volatile liquids with molar weights of  $10 \text{ g mol}^{-1}$  and  $40 \text{ g mol}^{-1}$  respectively. Two cotton plugs, one soaked in X and the other soaked in Y, are simultaneously placed at the ends of a tube of length  $L = 24 \text{ cm}$ , as shown in the figure. The tube is filled with an inert gas at 1 atmosphere pressure and a temperature of 300 K. Vapours of X and Y react to form a product which is first observed at a distance  $d \text{ cm}$  from the plug soaked in X. Take X and Y to have equal molecular diameters and assume ideal behaviour for the inert gas and the two vapours.



**Example 9 :**

The value of  $d$  in cm (shown in the figure), as estimated from Graham's law, is –

- (A) 8 (B) 12  
(C) 16 (D) 20

**Sol. (C).** From Graham's law,  $r \propto \frac{1}{\sqrt{M}}$

$$\frac{r_x}{r_y} = \sqrt{\frac{M_y}{M_x}} ; \frac{x}{24-x} = \sqrt{\frac{40}{10}}$$

$$\frac{x}{24-x} = 2 ; x = 16$$

**Example 10 :**

The experimental value of  $d$  is found to be smaller than the estimate obtained using Graham's law. This is due to –

- (A) Larger mean free path for X as compared to that of Y.  
(B) Larger mean free path for Y as compared to that of X.  
(C) Increased collision frequency of Y with the inert gas as compared to that of X with the inert gas.  
(D) Increased collision frequency of X with the inert gas as compared to that of Y with the inert gas.

**Sol. (D).**  $\lambda = \frac{1}{\sqrt{2}} \frac{RT}{\pi \sigma^2 PV}$

Increased collision frequency of X with the inert gas as compared to that of y with the inert gas. Therefore, the experimental value of  $d$  is found to be smaller than the estimate obtained using Graham's law.

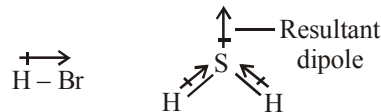
**Example 11 :**

What type(s) of intermolecular forces exist between the following pairs:

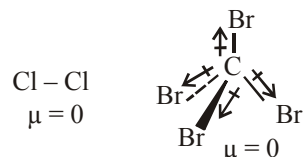
- (a) HBr and  $\text{H}_2\text{S}$  (b)  $\text{Cl}_2$  and  $\text{CBr}_4$   
(c)  $\text{I}_2$  and  $\text{NO}_3^-$  (d)  $\text{NH}_3$  and  $\text{C}_6\text{H}_6$

**Sol.** Classify the species into three categories: ionic, polar (possessing a dipole moment), and nonpolar. Keep in mind that dispersion forces exist between all species.

- (a) Both HBr and  $\text{H}_2\text{S}$  are polar molecules. Therefore, the intermolecular forces present are dipole-dipole forces, as well as dispersion forces.



- (b) Both  $\text{Cl}_2$  and  $\text{CBr}_4$  are nonpolar, so there are only dispersion forces between these molecules.



- (c)  $\text{I}_2$  is a homonuclear diatomic molecule and therefore nonpolar, so the forces between it and the ion  $\text{NO}_3^-$  are ion-induced dipole forces and dispersion forces.  
(d)  $\text{NH}_3$  is polar, and  $\text{C}_6\text{H}_6$  is nonpolar. The forces are dipole-induced dipole forces and dispersion forces.

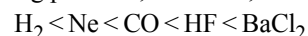
**Example 12 :**

List the substances  $\text{BaCl}_2$ ,  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{HF}$ , and  $\text{Ne}$  in order of increasing boiling point.

**Sol.** We need to assess the intermolecular forces in these substances and use that information to determine the relative boiling points.

The boiling point depends in part on the attractive forces in each substance. We need to order these according to the relative strengths of the different kinds of intermolecular attractions.

The attractive forces are stronger for ionic substances than for molecular ones, so  $\text{BaCl}_2$  should have the highest boiling point. The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are  $\text{H}_2(2)$ ,  $\text{CO}(28)$ ,  $\text{HF}(20)$ , and  $\text{Ne}(20)$ . The boiling point of  $\text{H}_2$  should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of  $\text{CO}$ ,  $\text{HF}$ , and  $\text{Ne}$  are similar. Because  $\text{HF}$  can hydrogen bond, however, it should have the highest boiling point of the three. Next is  $\text{CO}$ , which is slightly polar and has the highest molecular weight. Finally,  $\text{Ne}$ , which is nonpolar, should have the lowest boiling point of these three. The predicted order of boiling points is, therefore,



## QUESTION BANK

## CHAPTER 5 : STATES OF MATTER

## EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

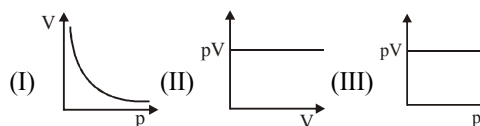
**PART-1 : INTERMOLECULAR FORCES**

- Q.1** Van der Waals' forces include  
 I. London forces.  
 II. chemical bonding forces.  
 III. dipole-dipole forces.  
 IV. dipole-induced dipole forces.  
 Which of the following option is correct?  
 (A) I, II and III (B) II, III and IV  
 (C) Only I and II (D) I, III and IV
- Q.2** Hydrogen bond is a special case of the  
 (A) dispersion force  
 (B) dipole-dipole interaction  
 (C) dipole-induced dipole interaction  
 (D) All of the above
- Q.3** The heat of vaporisation of  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CS}_2$  are 40.6, 38.6 and 26.8  $\text{kJ mol}^{-1}$  respectively. The order of decreasing intermolecular forces in these liquids is  
 (A)  $\text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > \text{CS}_2$   
 (B)  $\text{CS}_2 > \text{C}_2\text{H}_5\text{OH} > \text{H}_2\text{O}$   
 (C)  $\text{H}_2\text{O} > \text{CS}_2 > \text{C}_2\text{H}_5\text{OH}$   
 (D)  $\text{CS}_2 > \text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH}$
- Q.4** The term intermolecular forces does not include  
 I. electrostatic forces that exist between two oppositely charged ions.  
 II. covalent bond.  
 III. van der Waals' forces.  
 Choose the correct option.  
 (A) I and II (B) II and III  
 (C) I and III (D) I, II and III
- Q.5** Dipole-dipole interaction is stronger than the London forces but is weaker than ion-ion interaction because  
 (A) only partial charges are involved  
 (B) only total charges are involved  
 (C) Both (A) and (B)  
 (D) None of these
- Q.6** London force is a/an –  
 (A) attraction force that acts between two temporary dipoles.  
 (B) attraction force that acts between two permanent dipoles.  
 (C) repulsion force that acts between two permanent dipoles.  
 (D) repulsion force that acts between two temporary dipoles.

**PART-2 : THE GAS LAWS**

- Q.7** Equal weights of ethane and hydrogen are mixed in an empty container at  $25^\circ\text{C}$ . Determine the fraction of the total pressure exerted by hydrogen  
 (A) 16/30 (B) 15/16  
 (C) 30/16 (D) 16/15

- Q.8** The densities of  $\text{CH}_4$  and  $\text{O}_2$  are in the ratio 1 : 2. Calculate the ratio of rates of diffusion of oxygen and methane.  
 (A) 1.414 : 1 (B) 1 : 1.414  
 (C) 1.614 : 1 (D) 1.614 : 1
- Q.9** A gas occupies a volume of 2.4 litres at a pressure of 740mm of mercury. Keeping the temperature constant, calculate its volume at standard pressure  
 (A) 2.4 litres (B) 2.34 litres  
 (C) 2.5 litres (D) None of these
- Q.10** A gas occupies a volume of 580 ml at  $17^\circ\text{C}$ . It is heated to  $100^\circ\text{C}$  at constant pressure. Calculate the volume of the gas -  
 (A) 746 ml. (B) 760 ml.  
 (C) 773 ml. (D) 780 ml.
- Q.11** At constant temperature, in a given mass of an ideal gas  
 (A) The ratio of pressure & volume always remains constant.  
 (B) Volume always remains constant.  
 (C) Pressure always remains constant.  
 (D) The product of pressure & volume always remains constant.
- Q.12** Which of the following gas mixture is not applicable for Dalton's law of partial pressure  
 (A)  $\text{SO}_2$  and  $\text{Cl}_2$  (B)  $\text{CO}_2$  and  $\text{N}_2$   
 (C)  $\text{CO}$  and  $\text{CO}_2$  (D)  $\text{CO}$  and  $\text{N}_2$
- Q.13** The rate of diffusion of hydrogen gas is  
 (A) 1.4 times to He gas (B) Same as He gas  
 (C) 5 times to He gas (D) 2 times to He gas
- Q.14** Use of hot air balloons in sports and meteorological observations is an application of  
 (A) Boyle's law (B) Newton's law  
 (C) Kelvin's law (D) Charles' law
- Q.15** The pressure in well inflated tyres of automobiles is almost constant, but on a hot summer day this increases considerably and tyre may burst. This phenomena is explained by  
 (A) Boyle's law (B) Charles' law  
 (C) Gay Lussac's law (D) Avogadro law
- Q.16** Pressure of a mixture of 4 g of  $\text{O}_2$  and 2 g of  $\text{H}_2$  confined in a bulb of 1 L at  $0^\circ\text{C}$  is –  
 (A) 25.215 atm (B) 31.205 atm  
 (C) 45.215 atm (D) 15.210 atm.
- Q.17** Some graphs are given below.



- Which of the above graph represents Boyle's law?  
 (A) I and II (B) I and III  
 (C) II and III (D) I, II and III

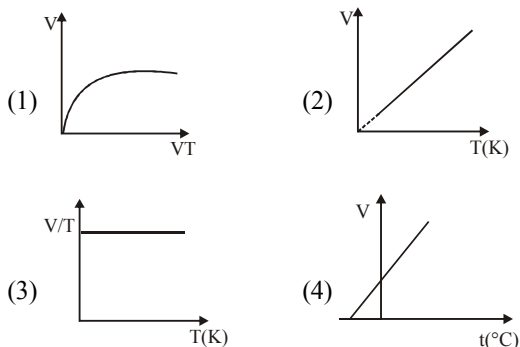
- Q.18** Avogadro's law is the combination of  
I. Charles' law.  
II. Boyle's law.  
III. Dalton's atomic theory.  
IV. Gay Lussac's law of combining volume.  
Select the correct option.

(A) I and II (B) II and III  
(C) III and IV (D) I and IV

- Q.19** If P, V & T represent pressure, volume and temperature of the gas, the correct representation of Boyle's law is  
(A)  $V \propto 1/P$  (P is constant)  
(B)  $PV = RT$   
(C)  $V \propto 1/P$  (at constant T)  
(D)  $PV = nRT$

**PART-3 : IDEAL GAS EQUATION**

- Q.20** Calculate the weight of  $CH_4$  in a 9 litre cylinder at 16 atm and  $27^\circ C$  ( $R = 0.08$  lit. atm/K) -  
(A) 96 gm (B) 86 gm  
(C) 80 gm (D) 90 gm
- Q.21** What is the density of sulphur dioxide ( $SO_2$ ) at STP -  
(A) 2.86 gm/lit. (B) 1.76 gm/lit  
(C) 1.86 gm/lit (D) None of these
- Q.22** How many litres would 5 moles of  $H_2$  occupy at  $25^\circ C$  and 2atm pressure -  
(A) 61.20 litres (B) 61.09 litres  
(C) 30.50 litres (D) 30.60 litres
- Q.23** Which of the following shows correct relation between volume and temperature for fixed mole of ideal gas at constant pressure -



(A) All correct (B) 1, 2, 3 are correct  
(C) 1, 2 are correct (D) 1, 3 are correct

- Q.24** In the equation of state of an ideal gas  $PV = nRT$ , the value of the universal gas constant would depend only on  
(A) The nature of the gas  
(B) The pressure of the gas  
(C) The units of the measurement  
(D) None of these
- Q.25** At  $25^\circ C$  and 760 mm of Hg pressure a gas occupies 600 mL volume. What will be its pressure at a height where temperature is  $10^\circ C$  and volume of the gas is 640 mL?  
(A) 677 mm Hg (B) 600 mm Hg  
(C) 700 mm Hg (D) 752 mm Hg

- Q.26** The number of moles of  $H_2$  in 0.224 L of hydrogen gas at STP ( $273$  K, 1 atm) assuming ideal gas behaviour is -  
(A) 1 (B) 0.1  
(C) 0.01 (D) 0.001

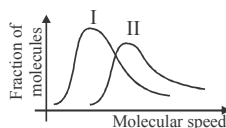
**PART-4 : KINETIC THEORY OF GASES**

- Q.27** A gaseous mixture contains 4 molecules with a speed of  $6$  cm  $sec^{-1}$ , 5 molecules with a speed of  $2$  cm  $sec^{-1}$  and 10 molecules with a speed of  $3$  cm  $sec^{-1}$ . What is the RMS speed of the gas -  
(A)  $2.5$  cm  $sec^{-1}$  (B)  $1.9$  cm  $sec^{-1}$   
(C)  $3.6$  cm  $sec^{-1}$  (D)  $4.6$  cm  $sec^{-1}$
- Q.28** Calculate the RMS speed of a gas with average speed  $45475$  cm/sec -  
(A)  $45475$  cm/sec. (B)  $92131$  cm/sec.  
(C)  $49360$  cm/sec (D)  $20259$  cm/sec
- Q.29** What is the temperature at which oxygen molecules have the same r.m.s. speed as the hydrogen molecules at  $27^\circ C$   
(A)  $3527^\circ C$  (B)  $4227^\circ C$   
(C)  $4527^\circ C$  (D)  $4000^\circ C$
- Q.30** Calculate the total kinetic energy in joules, of the molecules in 8 gm of methane at  $27^\circ C$ -  
(A)  $1770.5$  Joule (B)  $1870.5$  joule  
(C)  $1970.5$  joule (D)  $1670.5$  joule
- Q.31** Calculate the root mean square speed of  $SO_2$  at S.T.P. -  
(A)  $3.26 \times 10^4$  cm/sec (B)  $1.26 \times 10^2$  cm/sec  
(C)  $1.26 \times 10^4$  cm/sec (D)  $3.26 \times 10^2$  cm/sec
- Q.32** Internal energy and pressure of a gas per unit volume are related as

(A)  $P = \frac{2}{3} E$  (B)  $P = \frac{3}{2} E$   
(C)  $P = \frac{1}{2} E$  (D)  $P = 2E$

- Q.33** According to kinetic theory of gases, for a diatomic molecule  
(A) The pressure exerted by the gas is proportional to the mean speed of the molecules.  
(B) The pressure exerted by the gas is proportional to the root mean square speed of the molecules.  
(C) The root mean square speed is inversely proportional to the temperature.  
(D) The mean translational kinetic energy of the molecules is proportional to the absolute temperature.
- Q.34** 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
- Q.35** The r.m.s. speed of a certain gas is  $v$  at  $300$  K. The temperature, at which the r.m.s. speed becomes double  
(A)  $1200$  K (B)  $900$  K  
(C)  $600$  K (D)  $150$  K

- Q.36** With increase of pressure, the mean free path  
 (A) Decreases (B) Increases  
 (C) Does not change (D) Becomes zero
- Q.37** The ratio among most probable speed, mean speed and root mean square speed is given by  
 (A) 1 : 2 : 3 (B)  $1 : \sqrt{2} : \sqrt{3}$   
 (C)  $\sqrt{2} : \sqrt{3} : \sqrt{8/\pi}$  (D)  $\sqrt{2} : \sqrt{8/\pi} : \sqrt{3}$
- Q.38** The graphs representing distribution of molecular speeds at 300 K for gases  $\text{Cl}_2$  and  $\text{N}_2$  are as shown in figure (Atomic mass  $N = 14$ ,  $\text{Cl} = 35.5$ )



- (A) I graph is for  $\text{N}_2$  and II is for  $\text{Cl}_2$ .  
 (B) II graph is for  $\text{N}_2$  and I is for  $\text{Cl}_2$ .  
 (C) either graph can be taken for  $\text{N}_2$  or  $\text{Cl}_2$ .  
 (D) None of these
- Q.39** Choose the correct arrangement. The symbols have their usual meanings  
 (A)  $\bar{v} > u_{\text{mp}} > u_{\text{rms}}$  (B)  $u_{\text{rms}} > \bar{v} > u_{\text{mp}}$   
 (C)  $u_{\text{mp}} > \bar{v} > u_{\text{rms}}$  (D)  $u_{\text{mp}} > u_{\text{rms}} > \bar{v}$
- Q.40** The pressure exerted by the gas is due to  
 (A) the repulsion between gas molecules.  
 (B) the attraction between gas molecules.  
 (C) collision of the particles with the wall of the container.  
 (D) Both (A) and (B)
- Q.41** A vessel of 50 L capacity contains 0.5 mole of  $\text{O}_2$  at  $27^\circ\text{C}$  under a pressure of 2 atm. If half of the molecules of  $\text{O}_2$  are removed from the vessel then rms speed of  $\text{O}_2$  molecules will  
 (A) increase (B) decrease  
 (C) not change (D) first increase then decrease.

### PART-5 : REAL GASES

- Q.42** Gases deviate from the ideal gas behaviour because their molecules  
 (A) Possess negligible volume  
 (B) Have forces of attraction between them  
 (C) Are polyatomic  
 (D) Are not attracted to one another
- Q.43** A gas is found to have a formula  $[\text{CO}]_x$ . If its vapour density is 70, the value of x is  
 (A) 2.5 (B) 3.0  
 (C) 5.0 (D) 6.0
- Q.44** At high temperature and low pressure, the Vander Waal's equation is reduced to

- (A)  $\left(p + \frac{a}{V_m^2}\right)(V_m) = RT$  (B)  $pV_m = RT$   
 (C)  $p(V_m - b) = RT$  (D)  $\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$

- Q.45** One mole of  $\text{CO}_2$  occupying 0.4 litre at 300 K and 40 atm pressure is –  
 (A) less compressible  
 (B) more compressible  
 (C) ideal  
 (D) does not have a definite compressibility.
- Q.46** The real gases show an ideal behaviour when pressure approaches  
 (A) 10 atm (B) zero  
 (C) 100 atm (D) All of the these
- Q.47** In van der Waals equation of state for a real gas, the term that accounts for intermolecular forces is

- (A)  $V_m - b$  (B)  $P + \frac{a}{V_m^2}$   
 (C)  $RT$  (D)  $1/RT$

- Q.48** Which of the following expressions between the van der Waals constant, 'b' and the radius 'r' of spherical molecule is correct?

- (A)  $b = \left[\frac{4}{3}\pi r^3\right] N_A$  (B)  $b = \left[\frac{4}{3}\pi r^3\right]$   
 (C)  $b = 2\left[\frac{4}{3}\pi r^3\right] N_A$  (D)  $b = 4\left[\frac{4}{3}\pi r^3\right] N_A$

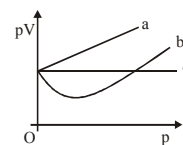
- Q.49** At low pressure, the van der Waals equation is reduced to –

- (A)  $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RTV_m}$  (B)  $Z = \frac{PV_m}{RT} = 1 + \frac{bP}{RT}$   
 (C)  $PV_m = RT$  (D)  $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RT}$

- Q.50** The compressibility factor of a gas is more than unity at STP. Its value of  $V_m$  is  
 (A) equal to  $22.4 \text{ dm}^3$   
 (B) dependent on its molecular size  
 (C) greater than  $22.4 \text{ dm}^3$   
 (D) lesser than  $22.4 \text{ dm}^3$

#### Directions (Q. Nos. 51-52)

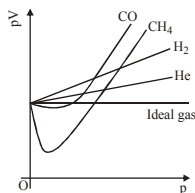
Answer the following questions, the plot of pV versus p at constant temperature is given below.



- Q.51** Which of the above slope shows an ideal gas behaviour?  
 (A) Only a (B) Only b  
 (C) Only c (D) a and b
- Q.52** Which of the above slope shows real gas behaviour?  
 (A) a and c (B) Only b  
 (C) a and b (D) a, b and c
- Q.53** Which of the following gases is expected to have largest value of van der Waals constant 'a' ?  
 (A) He (B)  $\text{H}_2$   
 (C)  $\text{NH}_3$  (D)  $\text{O}_2$

**Directions (Q. Nos. 54-55)**

Give the answers of the following questions on the basis of the graph which is given below.



**Q.54** Gases which show only positive deviation from ideal gas behaviour at high pressure

- (A) CO and CH<sub>4</sub> (B) H<sub>2</sub> and He  
(C) CO and He (D) CH<sub>4</sub> and H<sub>2</sub>

**Q.55** Which of the following gases show negative as well as positive deviation from the ideal gas behaviour?

- (A) H<sub>2</sub> and CH<sub>4</sub> (B) CO and He  
(C) CO and CH<sub>4</sub> (D) H<sub>2</sub>, He and CH<sub>4</sub>

**PART-6 : LIQUIFICATION OF GASES**

**Q.56** A gas can be liquefied

- (A) Above its critical temperature.  
(B) At its critical temperature.  
(C) Below its critical temperature.  
(D) At any temperature.

**Q.57** However great the pressure, a gas cannot be liquefied above its

- (A) Boyle temperature (B) Inversion temperature  
(C) Critical temperature (D) Room temperature

**Q.58** An ideal gas obeying kinetic theory of gases can be liquefied if

- (A) Its temperature is more than critical temperature T<sub>c</sub>  
(B) Its pressure is more than critical pressure P<sub>c</sub>  
(C) Its pressure is more than P<sub>c</sub> at a temperature less than T<sub>c</sub>  
(D) It cannot be liquefied at any value of P & T

**Q.59** NH<sub>3</sub> can be liquefied at ordinary temperature without the application of pressure. But O<sub>2</sub> cannot because

- (A) its critical temperature is very high.  
(B) its critical temperature is low.  
(C) its critical temperature is moderate.  
(D) its critical temp. is higher than that of NH<sub>3</sub>

**Q.60** The relationship between P<sub>c</sub>, V<sub>c</sub> and T<sub>c</sub> is –

- (A) P<sub>c</sub>V<sub>c</sub> = RT (B) P<sub>c</sub>V<sub>c</sub> = 3RT<sub>c</sub>  
(C) P<sub>c</sub>V<sub>c</sub> =  $\frac{3}{5}$ RT<sub>c</sub> (D) P<sub>c</sub>V<sub>c</sub> =  $\frac{3}{8}$ RT<sub>c</sub>

**Q.61** The values of T<sub>c</sub> of a few gases is given below.

H<sub>2</sub> : 33.2 K, O<sub>2</sub> : 154.3 K, He : 5.3 K and CO<sub>2</sub> : 304.10 K. What is the correct increasing order of liquefaction of above gases?

- (A) He < O<sub>2</sub> < H<sub>2</sub> < CO<sub>2</sub> (B) He < H<sub>2</sub> < O<sub>2</sub> < CO<sub>2</sub>  
(C) CO<sub>2</sub> < O<sub>2</sub> < H<sub>2</sub> < He (D) O<sub>2</sub> < CO<sub>2</sub> < H<sub>2</sub> < He

**PART-7 : LIQUID STATE**

**Q.62** Which one of the following is correct about surface tension (S.T) and viscosity (η) ?

- (A) Both increase with temperature.  
(B) Both decrease with temperature.  
(C) S.T. increases whereas η decreases with temperature.  
(D) S.T. decreases whereas η increases with temperature.

**Q.63** The normal boiling point and the standard boiling point of the water is respectively

- (A) 100°C and 0 K (B) 0°C and 100 K  
(C) 100°C and 99.6°C (D) 99.6°C and 100°C

**Q.64** Which of the following option is correct regarding partial pressure of gases when these are collected over water?

- (A) P<sub>dry</sub> = P<sub>total</sub> – surface tension  
(B) P<sub>dry</sub> = P<sub>total</sub> – osmotic pressure  
(C) P<sub>dry</sub> = P<sub>total</sub> – aqueous tension  
(D) P<sub>dry</sub> = P<sub>total</sub> – vapour pressure

**Q.65** The viscous force which acts between two layers is proportional to

- I. area of contact. II. speed gradient.

Identify the correct option.

- (A) Only I (B) Only II  
(C) Both I and II (D) Neither I nor II

**EXERCISE - 2 [LEVEL-2]**

**Choose one correct response for each question.**

**Q.1** What is the pressure of a mixture of 1 g of hydrogen and 1.4 g of nitrogen stored in a 5 litre vessel at 127 °C

- (A) 5.50 atm. (B) 3.61 atm.  
(C) 4.40 atm. (D) 4.50 atm.

**Q.2** 0.333 grams of alcohol displaced in a Victor Meyer apparatus 171 c.c. of air measured over water at 15 °C. The barometric pressure was 773 torr. Calculate the molecular weight of alcohol-

- (Aqueous tension at 15 °C = 13 torr.)  
(A) 33.34 g/ mol. (B) 28.80 g/ mol.  
(C) 46.0 g/ mol (D) 13.0 g/mol.

**Q.3** Atmospheric air contains 20% O<sub>2</sub> and 80% N<sub>2</sub> by volume and exerts a pressure of 760 mm. Calculate the partial pressure of each gas -

- (A) 152 mm, 608 mm (B) 608 mm, 152 mm  
(C) 760 mm both (D) None of these

**Q.4** 2.8 g of N<sub>2</sub>, 2.8 g CO, 4.4 g CO<sub>2</sub> are found to exert a pressure of 700 Torr. Find partial pressure of N<sub>2</sub> gas in the mixture -

- (A) 280.8 Torr (B) 233.3 Torr  
(C) 300 Torr (D) None of these

**Q.5** Calculate the relative rates of diffusion of <sup>235</sup>UF<sub>6</sub> and <sup>238</sup>UF<sub>6</sub> in the gaseous state (Atomic mass F = 19).

- (A) 1.0043 : 1.0000 (B) 1.0000 : 1.0043  
(C) 1.349 : 1.352 (D) 1.352 : 1.349

**Q.6** Calculate the molecular weight of a gas which diffuses through a porous plug at 1/6th of the speed of hydrogen under same conditions.

- (A) 36 (B) 76  
(C) 72 (D) 63

**Q.7** The vapour density of gas A is thrice that of the gas B. If the molecular weight of B is M, then calculate the molecular weight of A.

- (A) M (B) 3M  
(C) M/3 (D) None of these

**Q.8** Calculate average kinetic energy, in joules, of the molecules in 8.0 g of methane at 27°C -

- (A) 8169.75 Joules (B) 1869.75 Joules  
(C) 6189.57 Joules (D) 9186.57 Joules

**Q.9** A gas occupies 3 litres at 32°C and one atmospheric pressure. What volume will it occupy if the temperature is changed to 18 °C, the pressure remaining constant -

- (A) 2.91 litres (B) 2.86 litres  
(C) 2.30 litres (D) None of these

**Q.10** The density of a gas at -23°C and 780 torr is 1.40 gram per litre. Which one of the following gases is it -

- (A) CO<sub>2</sub> (B) SO<sub>2</sub>  
(C) Cl<sub>2</sub> (D) N<sub>2</sub>

**Q.11** 5gm of XeF<sub>4</sub> gas was introduced into a vessel of 6 litre capacity at 80°C. What is the pressure of the gas in atmosphere -

- (A) 0.21 atm (B) 0.31 atm  
(C) 0.11 atm (D) 0.41 atm.

**Q.12** Calculate the temperature at which 28 gm N<sub>2</sub> occupies a volume of 10 litre at 2.46 atm-

- (A) 300 K (B) 320 K  
(C) 340 K (D) 280 K

**Q.13** Densities of two gases are in the ratio 1 : 2 and their temperatures are in the ratio 2 : 1, then the ratio of their respective pressures is

- (A) 1 : 1 (B) 1 : 2  
(C) 2 : 1 (D) 4 : 1

**Q.14** At 25°C and 730 mm pressure, 380 mL of dry oxygen was collected. If the temperature is constant, what volume will the oxygen occupy at 760 mm pressure?

- (A) 365 mL (B) 449 mL  
(C) 569 mL (D) 621 mL

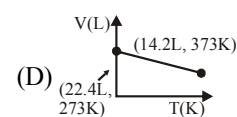
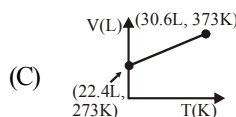
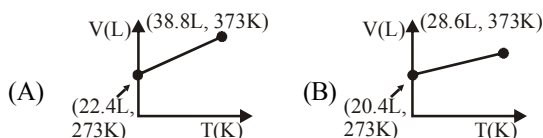
**Q.15** A sample of a given mass of gas at constant temperature occupies a volume of 95 cm<sup>3</sup> under a pressure of 9.962 × 10<sup>4</sup> Nm<sup>-2</sup>. At the same temperature its volume at pressure of 10.13 × 10<sup>4</sup> Nm<sup>-2</sup> is

- (A) 190 cm<sup>3</sup> (B) 93 cm<sup>3</sup>  
(C) 46.5 cm<sup>3</sup> (D) 4.75 cm<sup>3</sup>

**Q.16** The temperature of the gas is raised from 27°C to 927°C, the root mean square speed is

- (A) Three times the earlier value  
(B) same as before  
(C) halved  
(D) doubled.

**Q.17** Which of the following volume (V)-temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure?



**Q.18** At moderate pressure, compressibility factor of a gas –

- (A) increases with increase in temperature.  
(B) decreases with increase in temperature.  
(C) remains constant with change in temperature.  
(D) is greater than one.

**Q.19** The volume of 0.0168 mol of O<sub>2</sub> obtained by decomposition of KClO<sub>3</sub> and collected by displacement of water is 428 mL at a pressure of 754 mm Hg at 25°C. The pressure of water vapour at 25°C is –

- (A) 18 mm Hg (B) 20 mm Hg  
(C) 22 mm Hg (D) 24 mm Hg.

**Q.20** The kinetic energy of two moles of N<sub>2</sub> at 27°C is (R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>)

- (A) 5491.6 J (B) 6491.6 J  
(C) 7482.6 J (D) 8882.4 J

**Q.21** A 22 g chunk of dry ice is placed in a empty 600mL tightly closed vessel at 25°C. What would be the final pressure inside the vessel if all CO<sub>2</sub> gets evaporated?

- (A) 20.4 atm (B) 19.4 atm  
(C) 3.71 atm (D) 21.4 atm.

**Q.22** The rms speed of N<sub>2</sub> molecules in a gas is u. If the temperature is doubled and the nitrogen molecules dissociate into nitrogen atom, the rms speed becomes

- (A) u/2 (B) 2u  
(C) 4u (D) 14u

**Q.23** A neon-dioxygen mixture contains 70.6 g O<sub>2</sub> and 167.5 g neon. If pressure of the mixture of gases in the cylinder is 25 bar. What is the partial pressure of O<sub>2</sub> and Ne in the mixture respectively?

- (A) 5.25 bar, 10 bar (B) 19.75 bar, 5.25 bar  
(C) 19.75 bar, 10 bar (D) 5.25 bar, 19.75 bar

**Q.24** What will be the minimum pressure required to compress 2 Litre of gas at 1 bar to 1 Litre at 25°C?

- (A) 1 bar (B) 2 bar  
(C) 4 bar (D) 6 bar

**Q.25** Density of a gas is highest at

- (A) 100°C, 1 atm (B) 273°C, 1 atm  
(C) 0°C, 1 atm (D) 25°C, 1 atm.

**Q.26** Consider the equation  $Z = \frac{PV}{nRT}$ ; which of the following statements is correct?

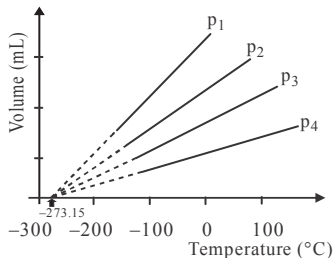
- (A) When  $Z > 1$ , real gases are easier to compress than the ideal gas.  
(B) When  $Z = 1$ , real gases get compressed easily.  
(C) When  $Z > 1$ , real gases are difficult to compress  
(D) When  $Z = 1$ , real gases are difficult to compress.

**Q.27** If most probable speed is represented by  $\alpha$  and fraction possessing it by  $f$ , then with increase in temperature which one of the following is correct?

- (A)  $\alpha$  increases,  $f$  decreases (B)  $\alpha$  decreases,  $f$  increases  
(C) Both  $\alpha$  and  $f$  decreases (D) Both  $\alpha$  and  $f$  increases

- Q.28** The density of air is 0.00130 g/mL. The vapour density of air will be  
 (A) 0.00065 (B) 0.65  
 (C) 14.4816 (D) 14.56

For Q.29-Q.31 : Consider the following figure.



- Q.29** The above graph explains  
 (A) Boyle's law (B) Avogadro's law  
 (C) Charles' law (D) Graham's law
- Q.30** Each line of the volume versus temperature graph is called \_\_\_\_\_.  
 (A) isotherm (B) isobar  
 (C) isochore (D) All of the above
- Q.31** Arrange the pressures  $p_1$ ,  $p_2$ ,  $p_3$  and  $p_4$  in the increasing order which are shown in the graphs.  
 (A)  $p_1 < p_2 < p_3 < p_4$  (B)  $p_4 < p_3 < p_2 < p_1$   
 (C)  $p_1 = p_2 = p_3 = p_4$  (D)  $p_4 = p_3 < p_2 = p_1$
- Q.32** A 2.24 L cylinder of oxygen at N.T.P. is found to develop a leakage. When the leakage was plugged, the pressure dropped to 570 mm of Hg. The number of moles of gas that escaped will be  
 (A) 0.025 (B) 0.050  
 (C) 0.075 (D) 0.09
- Q.33** The density of a gas at 100 kPa is 0.1 g dm<sup>-3</sup>. Its root mean square speed will be  
 (A) 1414 m/s (B) 1732 m/s  
 (C) 707 m/s (D) 866 m/s

- Q.34** The density of methane at 2.0 atm pressure and 27°C is  
 (A) 0.13 g L<sup>-1</sup> (B) 0.26 g L<sup>-1</sup>  
 (C) 1.30 g L<sup>-1</sup> (D) 26.0 g L<sup>-1</sup>

- Q.35** A closed vessel contains equal number of molecules of N<sub>2</sub> and O<sub>2</sub> at a total pressure of 650 mm. If N<sub>2</sub> is completely removed the pressure will

- (A) drop to 650/3 (B) drop to 650/2  
 (C) remain unchanged (D) become 650 × 2

- Q.36** The average speed of an ideal gas molecule at 300 K is 2 m/s. The average speed at 1200 K will be

- (A) 6 m/s (B) 4 m/s  
 (C) 2 m/s (D) 8 m/s

- Q.37** A flask of capacity one litre is heated from 25°C to 35°C. What volume of air will escape from the flask?

- (A) 33 mL (B) 330 mL  
 (C) 3 mL (D) 0.33 mL

- Q.38** Two moles of N<sub>2</sub> gas in a 50 L vessel at STP shows –

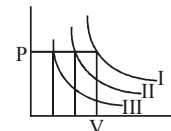
- (A) positive deviation  
 (B) negative deviation  
 (C) ideal gas behaviour  
 (D) first positive then negative deviation.

- Q.39** 0.40 g of helium in a bulb at a temperature of T K had a pressure of P atm. When the bulb was immersed in hotter bath at temperature 50 K more than the first one, 0.08 g of gas had to be removed to restore the original pressure. T is –

- (A) 100 K (B) 200 K  
 (C) 300 K (D) 500 K

- Q.40** I, II, III are three isotherms respectively at T<sub>1</sub>, T<sub>2</sub> and T<sub>3</sub>. Temperature will be in order

- (A) T<sub>1</sub> = T<sub>2</sub> = T<sub>3</sub> (B) T<sub>1</sub> < T<sub>2</sub> < T<sub>3</sub>  
 (C) T<sub>1</sub> > T<sub>2</sub> > T<sub>3</sub> (D) T<sub>1</sub> > T<sub>2</sub> = T<sub>3</sub>



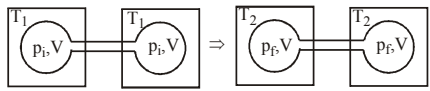


## EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

**NOTE:** The answer to each question is a NUMERICAL VALUE.

- Q.1** By how many times the absolute temperature of a gas when  $U_{\text{rms}}$  of a gas in a container of fixed volume is .....  $^4 \text{ cm/sec}$  to  $10 \times 10^4 \text{ cm/sec}$ .
- Q.2** My weight is 80 kg. I want to fly in the sky with the aid of balloons each containing 50 moles of  $\text{H}_2$  gas at 0.05 atm pressure and  $27^\circ\text{C}$  temperature. If the density of air at the given condition is 1.25 gm/lit, how many such type of balloons do I need to attach with myself to fly in the sky ?
- Q.3** Mixture of helium and oxygen are used in scuba diving tanks to help prevent "the bends." For a particular dive 46 L of  $\text{O}_2$  at  $25^\circ\text{C}$  and 1.0 atm was pumped along with 12L of He at  $25^\circ\text{C}$  and 1.0 atm into a tank with a volume of 5.0L. The partial pressure of each gas and the total pressure in the tank at  $25^\circ\text{C}$  is  $(10.7 + A)$  atm. Find the value of A.
- Q.4** Aqueous lithium hydroxide solution is used to purify air in spacecrafts and submarines because it absorbs carbon dioxide according to the equation
- $$2\text{LiOH}(\text{aq}) + \text{CO}_2(\text{g}) \longrightarrow \text{Li}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O}(\ell)$$
- The pressure of carbon dioxide in a cabin having a volume of  $2.4 \times 10^5 \text{ L}$  is  $7.9 \times 10^{-3} \text{ atm}$  at 312 K. A solution of lithium hydroxide ( $\text{LiOH}$ ) of negligible volume is introduced into the cabin. Eventually the pressure of  $\text{CO}_2$  is reduced to  $1.2 \times 10^{-4} \text{ atm}$ . If  $5.4 \times 10^A$  grams of lithium carbonate is formed by this process then find the value of A.
- Q.5** Using van der Waals equation, find the integral value of constant 'a' when two moles of a gas confined in a four litre flask exerts a pressure of 11.0 atm at a temperature of 300K. The value of 'b' for the gas is  $0.05 \text{ L mol}^{-1}$ .
- Q.6** Calculate the integral part of volume (in litres) occupied by 7.40g of  $\text{NH}_3$  at STP.
- Q.7** One mole of nitrogen gas at 0.8 atm takes 38s to diffuse through a pinhole, whereas one mole of unknown compound of xenon and fluorine at 1.6 atm takes 56.2 s to diffuse through the same hole. The molecular formula of the compound is  $\text{XeF}_n$ . (Atomic mass of Xe = 131). Find the value of n.
- Q.8** Freon-12 (the common name for the compound  $\text{CCl}_2\text{F}_2$ ) is widely used in refrigeration systems. Consider a 1.53L sample of gaseous  $\text{CCl}_2\text{F}_2$  at a pressure of  $5.6 \times 10^3 \text{ Pa}$ . If the pressure is changed to  $1.5 \times 10^4 \text{ Pa}$  at a constant temperature, The new volume of the gas is  $57 \times 10^{-A}$ . Find the value of A.
- Q.9** When 2g of a gaseous substance A is introduced into an initially evacuated flask at  $25^\circ\text{C}$ , the pressure is found to be 1atm. 3g of another gaseous substance B is then added to it at the same temperature and pressure. The final pressure is found to be 1.5atm. Calculate the ratio of molecular masses of B and A assuming ideal gas behaviour.
- Q.10** Sodium azide ( $\text{NaN}_3$ ) is used in some automobile air bags. The impact of a collision triggers the decomposition of  $\text{NaN}_3$  as follows:  $2\text{NaN}_3(\text{s}) \rightarrow 2\text{Na}(\text{s}) + 3\text{N}_2(\text{g})$
- The nitrogen gas produced quickly inflates the bag between the driver and the windshield. The volume of  $\text{N}_2$  generated at  $80^\circ\text{C}$  and 823mm Hg by the decomposition of 60.0g of  $\text{NaN}_3$  is  $(30.9 + A)$  litre. Find the value of A.
- Q.11** A sample of methane gas that has a volume of 3.8L at  $5^\circ\text{C}$  is heated to  $86^\circ\text{C}$  at constant pressure. Calculate its new volume (approximately in litre).
- Q.12** Calculate the temperature (in K) at which the root mean square speed of  $\text{SO}_2$  molecules is the same as that of oxygen at  $27^\circ\text{C}$ .

**EXERCISE - 4 [PREVIOUS YEARS AIEEE / JEE MAIN QUESTIONS]**

- Q.1** The no. of moles per litre in the equation  $PV = nRT$  is expressed by - [AIEEE-2002]  
 (A)  $\frac{P}{RT}$  (B)  $\frac{PV}{RT}$  (C)  $\frac{RT}{PV}$  (D) None
- Q.2** The correct value of R is - [AIEEE-2002]  
 (A)  $R = 0.082$  litre-atm  
 (B)  $R = 8.314 \times 10^7$  erg -  $K^{-1} \text{ mol}^{-1}$   
 (C)  $R = 2 K^{-1} \text{ mol}^{-1}$   
 (D) None
- Q.3** According to the kinetic theory of gases, in an ideal gas, between two successive collisions a gas molecule travels [AIEEE 2003]  
 (A) In a straight line path  
 (B) With an accelerated velocity  
 (C) In a circular path  
 (D) In a wavy path
- Q.4** As the temperature is raised from  $20^\circ\text{C}$  to  $40^\circ\text{C}$ , the average kinetic energy of neon atoms changes by a factor of which of the following? [AIEEE-2004]  
 (A)  $1/2$  (B)  $\sqrt{(313/293)}$   
 (C)  $313/293$  (D) 2
- Q.5** In van der Waals equation of state of the gas law, the constant 'b' is a measure of - [AIEEE-2004]  
 (A) intermolecular repulsions  
 (B) intermolecular attraction  
 (C) volume occupied by the molecules  
 (D) intermolecular collisions per unit volume
- Q.6** Which one of the following statements is not true about the effect of an increase in temperature on the distribution of molecular speeds in a gas? [AIEEE-2005]  
 (A) The fraction of the molecules with the most probable speed increases.  
 (B) The most probable speed increases.  
 (C) The area under the distribution curve remains the same as under the lower temperature.  
 (D) The distribution becomes broader.
- Q.7** Equal masses of methane and oxygen are mixed in an empty container at  $25^\circ\text{C}$ . The fraction of the total pressure exerted by oxygen is - [AIEEE-2007]  
 (A)  $\frac{2}{3}$  (B)  $\frac{1}{3} \times \frac{273}{298}$   
 (C)  $1/3$  (D)  $1/2$
- Q.8** If  $10^{-4} \text{ dm}^3$  of water is introduced into a  $1.0 \text{ dm}^3$  flask to 300 K, how many moles of water are in the vapour phase when equilibrium is established?  
 (Given : Vapour pressure of  $\text{H}_2\text{O}$  at 300 K is 3170 Pa ;  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ) [AIEEE 2010]  
 (A)  $5.56 \times 10^{-3} \text{ mol}$  (B)  $1.53 \times 10^{-2} \text{ mol}$   
 (C)  $4.46 \times 10^{-2} \text{ mol}$  (D)  $1.27 \times 10^{-3} \text{ mol}$
- Q.9** a and b are van der Waals' constants for gases. Chlorine is more easily liquefied than ethane because : [AIEEE 2011]  
 (A) a and b for  $\text{Cl}_2 > a$  and b for  $\text{C}_2\text{H}_6$   
 (B) a and b for  $\text{Cl}_2 < a$  and b for  $\text{C}_2\text{H}_6$   
 (C) a and  $\text{Cl}_2 < a$  for  $\text{C}_2\text{H}_6$  but b for  $\text{Cl}_2 > b$  for  $\text{C}_2\text{H}_6$   
 (D) a for  $\text{Cl}_2 > a$  for  $\text{C}_2\text{H}_6$  but b for  $\text{Cl}_2 < b$  for  $\text{C}_2\text{H}_6$
- Q.10** The compressibility factor for a real gas at high pressure is [AIEEE 2012]  
 (A)  $1 + RT/pb$  (B) 1  
 (C)  $1 + pb/RT$  (D)  $1 - pb/RT$
- Q.11** 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)  $C^* : \bar{C} : C = 1.225 : 1.128 : 1$   
 (B)  $C^* : \bar{C} : C = 1.128 : 1.225 : 1$   
 (C)  $C^* : \bar{C} : C = 1 : 1.128 : 1.225$   
 (D)  $C^* : \bar{C} : C = 1 : 1.225 : 1.128$
- Q.12** If Z is a compressibility factor, van der Waals equation at low pressure can be written as - [JEE MAIN 2014]  
 (A)  $Z = 1 - \frac{Pb}{RT}$  (B)  $Z = 1 + \frac{Pb}{RT}$   
 (C)  $Z = 1 + \frac{RT}{Pb}$  (D)  $Z = 1 - \frac{a}{VRT}$
- Q.13** Two closed bulbs of equal volume (V) containing an ideal gas initially at pressure  $p_i$  and temperature  $T_1$  are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to  $T_2$ . The final pressure  $p_f$  is: [JEE MAIN 2016]
- 
- (A)  $2p_i \left( \frac{T_1}{T_1 + T_2} \right)$  (B)  $2p_i \left( \frac{T_2}{T_1 + T_2} \right)$   
 (C)  $2p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right)$  (D)  $p_i \left( \frac{T_1 T_2}{T_1 + T_2} \right)$
- Q.14** 0.5 moles of gas A and x moles of gas B exert a pressure of 200 Pa in a container of volume  $10 \text{ m}^3$  at 1000 K. given R is the gas constant in  $\text{JK}^{-1} \text{ mol}^{-1}$ , x is : [JEE MAIN 2019 (JAN)]  
 (A)  $\frac{2R}{4+R}$  (B)  $\frac{2R}{4-R}$   
 (C)  $\frac{4-R}{2R}$  (D)  $\frac{4+R}{2R}$

- Q.15** Consider the van der Waals constants,  $a$  and  $b$ , for the following gases. [JEE MAIN 2019 (APRIL)]

Gas	Ar	Ne	Kr	Xe
$a / (\text{atm dm}^6 \text{ mol}^{-2})$	1.3	0.2	5.1	4.1
$b / (10^{-2} \text{ dm}^3 \text{ mol}^{-1})$	3.2	1.7	1.0	5.0

Which gas is expected to have the highest critical temperature?

- (A) Kr (B) Ne  
(C) Ar (D) Xe
- Q.16** At a given temperature  $T$ , gases Ne, Ar, Xe and Kr are found to deviate from ideal gas behaviour. Their equation of state is given as  $p = \frac{RT}{V-b}$  at  $T$ . Here,  $b$  is the van der Waals constant. Which gas will exhibit steepest increase in the plot of  $Z$  (compression factor) vs  $p$ ?

[JEE MAIN 2019 (APRIL)]

- (A) Ne (B) Ar  
(C) Xe (D) Kr

- Q.17** Consider the following table :

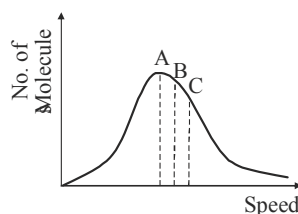
Gas	$a / (\text{k Pa dm}^6 \text{ mol}^{-1})$	$b / (\text{dm}^3 \text{ mol}^{-1})$
A	642.32	0.05196
B	155.21	0.04136
C	431.91	0.05196
D	155.21	0.4382

$a$  and  $b$  are vander waals constant. The correct statement about the gases is : [JEE MAIN 2019 (APRIL)]

- (A) Gas C will occupy lesser volume than gas A; gas B will be lesser compressible than gas D  
(B) Gas C will occupy more volume than gas A; gas B will be lesser compressible than gas D  
(C) Gas C will occupy more volume than gas A; gas B will be more compressible than gas D  
(D) Gas C will occupy lesser volume than gas A; gas B will be more compressible than gas D

- Q.18** The relative strength of interionic/intermolecular forces in decreasing order is : [JEE MAIN 2020 (JAN)]

- (A) Dipole – Dipole > Ion – Ion > Dipole – Ion  
(B) Ion – Ion > Dipole – Dipole > Dipole – Ion  
(C) Dipole – Ion > Dipole – Dipole > Ion – Ion  
(D) Ion – Ion > Dipole – Ion > Dipole – Dipole



Select the correct options : [JEE MAIN 2020 (JAN)]

- (A)  $A = V_{mp}$ ,  $B = V_{avg}$ ,  $C = V_{rms}$   
(B)  $A = V_{avg}$ ,  $B = V_{mp}$ ,  $C = V_{rms}$   
(C)  $A = V_{rms}$ ,  $B = V_{avg}$ ,  $C = V_{mp}$   
(D)  $A = V_{mp}$ ,  $B = V_{rms}$ ,  $C = V_{avg}$
- Q.20** The predominant intermolecular forces present in ethyl acetate, a liquid, are : [JEE MAIN 2020 (JAN)]
- (A) Hydrogen bonding and London dispersion  
(B) dipole-dipole and Hydrogen bonding.  
(C) London dispersion and dipole-dipole.  
(D) London dispersion, dipole-dipole and hydrogen bonding.

**EXERCISE - 5 (PREVIOUS YEARS AIPMT/NEET EXAM QUESTIONS)**

Choose one correct response for each question.

- Q.1** The surface tension of which of the following liquid is maximum— [AIPMT 2005]  
 (A)  $C_2H_5OH$  (B)  $CH_3OH$   
 (C)  $H_2O$  (D)  $C_3H_6$
- Q.2** If a gas expands at constant temperature, it indicates that: [AIPMT 2008]  
 (A) Number of the molecules of gas increases  
 (B) Kinetic energy of molecules decreases  
 (C) Pressure of the gas increases  
 (D) Kinetic energy of molecules remains the same
- Q.3** Volume occupied by one molecule of water (density =  $1g\ cm^{-3}$ ) is : [AIPMT 2008]  
 (A)  $5.5 \times 10^{-23}\ cm^3$  (B)  $9.0 \times 10^{-23}\ cm^3$   
 (C)  $6.023 \times 10^{-23}\ cm^3$  (D)  $3.0 \times 10^{-23}\ cm^3$
- Q.4** The energy absorbed by each molecule ( $A_2$ ) of a substance is  $4.4 \times 10^{-19}\ J$  and bond energy per molecule is  $4.0 \times 10^{-19}\ J$ . The kinetic energy of the molecule per atom will be: [AIPMT 2009]  
 (A)  $2.2 \times 10^{-19}\ J$  (B)  $2.0 \times 10^{-19}\ J$   
 (C)  $4.0 \times 10^{-20}\ J$  (D)  $2.0 \times 10^{-20}\ J$
- Q.5** The pressure exerted by 6.0g of methane gas in a  $0.03m^3$  vessel at  $129^\circ C$  is [Atomic masses : C = 12.01, H = 1.01 and  $R = 8.314\ J\ K^{-1}\ mol^{-1}$ ] [AIPMT (MAINS) 2010]  
 (A) 215216 Pa (B) 13409 Pa  
 (C) 41648 Pa (D) 31684 Pa
- Q.6** By what factors does the average speed of a gaseous molecule increase when the temperature (in Kelvin) is doubled? [AIPMT (PRE) 2011]  
 (A) 1.4 (B) 2.0  
 (C) 2.8 (D) 4.0
- Q.7** Two gases A and B having the same volume diffuse through a porous partition in 20 and 10 seconds respectively. The molecular mass of A is 49 u. Molecular mass of B will be [AIPMT (PRE) 2011]  
 (A) 25.00 u (B) 50.00 u  
 (C) 12.25 u (D) 6.50 u
- Q.8** A gaseous mixture was prepared by taking equal mole of CO and  $N_2$ . If the total pressure of the mixture was found 1 atmosphere, the partial pressure of the nitrogen ( $N_2$ ) in the mixture is [AIPMT (PRE) 2011]  
 (A) 1 atm (B) 0.5 atm  
 (C) 0.8 atm (D) 0.9 atm
- Q.9** A bubble of air is underwater at temperature  $15^\circ C$  and the pressure 1.5 bar. If the bubble rises to the surface where the temperature is  $25^\circ C$  and the pressure is 1.0 bar, what will happen to the volume of the bubble ? [AIPMT (MAINS) 2011]  
 (A) Volume will become greater by a factor of 1.6.  
 (B) Volume will become greater by a factor of 1.1.  
 (C) Volume will become smaller by a factor of 0.70.  
 (D) Volume will become greater by a factor of 2.5.
- Q.10** 50 mL of each gas A and of gas B takes 200 and 150 seconds respectively for effusing through a pin hole under the similar condition. If molecular mass of gas B is 36, the molecular mass of gas A will be : [AIPMT (PRE) 2012]  
 (A) 96 (B) 128  
 (C) 32 (D) 64
- Q.11** A certain gas takes three times as long to effuse out as helium. Its molecular mass will be : [AIPMT (MAINS) 2012]  
 (A) 27 u (B) 36 u  
 (C) 64 u (D) 9 u
- Q.12** For real gases van der Waals equation is written as :  

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$
 where 'a' and 'b' are van der Waals constants. Two sets of gases are :  
 (I)  $O_2, CO_2, H_2$  and He (II)  $CH_4, O_2$  and  $H_2$   
 The gases given in set-I in increasing order of 'b' and gases given in set-II in decreasing order of 'a', are arranged below. Select the correct order from the following : [AIPMT (MAINS) 2012]  
 (A) (I)  $He < H_2 < CO_2 < O_2$ , (II)  $CH_4 > H_2 > O_2$   
 (B) (I)  $O_2 < He < H_2 < CO_2$ , (II)  $H_2 > O_2 > CH_4$   
 (C) (I)  $H_2 < He < O_2 < CO_2$ , (II)  $CH_4 > O_2 > H_2$   
 (D) (I)  $H_2 < O_2 < He < CO_2$ , (II)  $O_2 > CH_4 > H_2$
- Q.13** Maximum deviation from ideal gas is expected from – [NEET 2013]  
 (A)  $NH_3(g)$  (B)  $H_2(g)$   
 (C)  $N_2(g)$  (D)  $CH_4(g)$
- Q.14** Dipole induced dipole interactions are present in which of the following pairs – [NEET 2013]  
 (A)  $SiF_4$  and He atoms (B)  $H_2O$  and alcohol  
 (C)  $Cl_2$  and  $CCl_4$  (D) HCl and He atoms
- Q.15** A gas such as carbon monoxide would be most likely to obey the ideal gas law at : [RE-AIPMT 2015]  
 (A) high temperatures and high pressures.  
 (B) low temperatures and low pressures.  
 (C) high temperatures and low pressures.  
 (D) low temperatures and high pressures.
- Q.16** Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape? [NEET 2016 PHASE 1]  
 (A) 1/8 (B) 1/4  
 (C) 3/8 (D) 1/2
- Q.17** Given van der Waals constant for  $NH_3, H_2, O_2$  and  $CO_2$  are respectively 4.17, 0.244, 1.36 and 3.59, which one of the following gases is most easily liquefied? [NEET 2018]  
 (A)  $O_2$  (B)  $H_2$   
 (C)  $NH_3$  (D)  $CO_2$
- Q.18** The correction factor 'a' to the ideal gas equation corresponds to [NEET 2018]  
 (A) Electric field present between the gas molecules.  
 (B) Volume of the gas molecules.  
 (C) Density of the gas molecules.  
 (D) Forces of attraction between the gas molecules.

**Q.19** A gas at 350 K and 15 bar has molar volume 20 percent smaller than that for an ideal gas under the same conditions. The correct option about the gas and its compressibility factor ( $Z$ ) is : [NEET 2019]

- (A)  $Z > 1$  and attractive forces are dominant.  
 (B)  $Z > 1$  and repulsive forces are dominant.  
 (C)  $Z < 1$  and attractive forces are dominant.  
 (D)  $Z < 1$  and repulsive forces are dominant.

## ANSWER KEY

EXERCISE - 1																									
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	D	B	A	A	A	A	B	B	B	A	D	A	A	D	C	A	D	C	C	A	A	B	A	C	A
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	C	C	C	B	A	A	D	C	A	A	D	B	B	C	C	B	C	B	B	B	B	D	A	C
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65										
A	C	C	C	B	C	C	C	D	B	D	B	B	C	C	C										

EXERCISE - 2																									
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	B	C	A	B	A	C	B	B	B	D	C	A	A	A	B	D	C	A	D	C	D	B	D	B	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40										
A	C	A	D	C	B	A	A	B	C	B	B	A	A	B	C										

EXERCISE - 3												
Q	1	2	3	4	5	6	7	8	9	10	11	12
A	4	3	1	3	6	9	6	2	3	6	5	600

EXERCISE - 4																				
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
A	A	B	A	C	C	A	C	D	D	C	C	D	B	C	A	C	C	D	A	C

EXERCISE - 5																			
Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
A	C	D	D	D	C	A	C	B	A	D	B	C	A	D	C	A	C	D	C

## STATES OF MATTER

### SOLUTIONS TRY IT YOURSELF-1

(1)  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ , where  $P_1 = 760 \text{ mm}$ ,  $V_1 = 320 \text{ cm}^3$ ,  
 $T_1 = 273 \text{ K}$  and  $P_2 = 600 \text{ mm}$ ;  $T_2 = 273 + 47 = 320 \text{ K}$ ;  $V_2 = ?$

$$\frac{760 \times 320}{273} = \frac{600 \times V_2}{320}$$

$$V_2 = \frac{760 \times 320 \times 320}{600 \times 273} = 475.12 \text{ cm}^3$$

(2) (C).  $PV = nRT$

$$2 \text{ atm} \times 44.8 \text{ litre} = \frac{246}{3x} \times 0.0821 \text{ lit atm K}^{-1} \text{ mol}^{-1} \times 546$$

$$\text{Atomic weight, } x = 41$$

(3)  $PV = nRT$

$$n = \frac{PV}{RT} = \frac{1 \times 0.5}{0.0821 \times 300} = 2.03 \times 10^{-2} \text{ mol}$$

(4) Calculation of partial pressure of  $\text{N}_2$  after mixing

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{250 \times 200}{300} = 166.6 \text{ mm}$$

Calculation of partial pressure of  $\text{H}_2$  after mixing

$$P_1 V_1 = P_2 V_2$$

$$P_2 = \frac{P_1 V_1}{V_2} = \frac{300 \times 350}{300} = 350 \text{ mm}$$

Total pressure ( $P$ ) =  $P_1 + P_2 = 166.6 + 350 = 516.6 \text{ mm Hg}$

(5)  $\frac{r(\text{fluoride})}{r(\text{nitrogen})} = \sqrt{\frac{M(\text{N}_2)}{M(\text{fluoride})}}$

$$\frac{1}{2.12} = \sqrt{\frac{28}{M(\text{fluoride})}}; \left(\frac{1}{2.12}\right)^2 = \frac{28}{M(\text{fluoride})}$$

$$M(\text{fluoride}) = 126$$

Further as the molecule contains one phosphorous atom

$$31 + 19x = 126 \Rightarrow x = 5$$

So, the formula of the compound must be  $\text{PF}_5$ .

(6) (C).  $d = \frac{PM}{RT}$ ;  $\frac{P_A}{P_B} = \frac{d_A}{d_B} \times \frac{M_B}{M_A} = 6$ ;  $P_A : P_B = 6 : 1$

(7) (D) (8) (A)

(9) (D) (10) (A)

(11) (A).  $\frac{PV_1}{RT} = \frac{(P/4) \times V_2}{R \times 2T} \Rightarrow V_2 = 8V_1$   
 $r_2 = 2r_1$  ( $\because V \propto r^3$ )

(12)  $M = \frac{dRT}{P} = \frac{3.43 \times 0.0821 \times 300}{1} = 84.48$

### TRY IT YOURSELF-2

(1)  $PV = \frac{w}{M} RT$

$$\frac{750}{760} \times 5 = \frac{6.431}{32} \times 0.0821 \times T$$

$$T = 299.0514 \text{ K}$$

$$u = \sqrt{\frac{3 \times 8.314 \times 10^7 \times 299.051}{32}} = 4.83 \times 10^4 \text{ cm s}^{-1}$$

(2)  $u(\text{O}_2) = \sqrt{\frac{3R \times 273}{32}}$ ;  $u(\text{CO}_2) = \sqrt{\frac{3R \times T}{44}}$

Both are given to be equal

$$\frac{3R \times 273}{32} = \frac{3RT}{44}$$

$$T = 375.38 \text{ K}$$

(3) (C)

(4) (C)

(5) (B)

(6) (C).  $U_{\text{rms}} = \sqrt{\frac{3RT}{M}}$

$$\frac{(U_{\text{rms}})_{\text{H}_2}}{(U_{\text{rms}})_{\text{O}_2}} = \sqrt{\frac{50}{2} \times \frac{32}{800}} = 1$$

(7) (B).  $\text{Br}_2$  molar mass = 160

$$T = 527^\circ\text{C} + 273^\circ\text{C}, T = 800 \text{ K}$$

$$(U_{\text{MPS}})_{\text{Br}_2} = (U_{\text{MPS}})_{\text{C}_n\text{H}_{2n-2}}$$

$$\left(\sqrt{\frac{2RT}{M}}\right)_{\text{Br}_2} = \left(\sqrt{\frac{2RT}{M}}\right)_{\text{series member}}$$

$$\left(\frac{T}{M}\right)_{\text{Br}_2} = \left(\frac{T}{M}\right)_{\text{series member}}$$

$$\frac{800}{160} = \left(\frac{200}{40}\right)_{\text{CH}\equiv\text{C}-\text{CH}_3}$$

Second member

Temperature for member (K) = Molar mass  $\times 5$

For second member  $t = -73^\circ\text{C}$

(8) (D).  $u_{\text{rms}_A} = \sqrt{\frac{3RT}{M_A}} = u_{\text{mp}_B} = \sqrt{\frac{2RT/2}{M_B}}$

$$\frac{3T}{M_A} = \frac{T}{M_B} ; \frac{M_A}{M_B} = \frac{3}{1}$$

(9) (BC)

(10) (D)

(11) (B).  $C_V = 3R + 9R = 12R$  ;  $C_P = 13R$

$$\gamma = \frac{C_p}{C_v} = \frac{13}{12}$$

### TRY IT YOURSELF-3

(1) (C)

(2) (C)

(3) (C). For non-polar gas Vander waal's constant  $a \uparrow$  if intermolecular forces  $\uparrow$

$$a_{\text{H}_2} < a_{\text{N}_2} < a_{\text{O}_2}$$

(4) (A).  $PV = Z.nRT$

$$1 \text{ atm} \times 20 \text{ litre} = Z \cdot \frac{30}{32} \times 0.0821 \times 273$$

$$Z = 0.951$$

$Z < 1$  attractive forces dominants.

(5) (D)

(6) (BC)

(7) (C). For positive deviation :  $PV = nRT + nP_b$

$$\Rightarrow \frac{PV}{nRT} = 1 + \frac{P_b}{RT}$$

Thus, the factor  $nP_b$  is responsible for increasing the PV value, above ideal value.  $b$  is actually the effective volume of molecule. So, it is the finite size of molecules that leads to the origin of  $b$  and hence positive deviation at high pressure.

(8) (ACD). At very large molar volume

$$P + \frac{a}{V_m^2} = P \text{ and } V_m - b = V_m$$

At low pressure, when the sample occupies a large volume, the molecules are so far apart for most of the time that the intermolecular forces play no significant role, and the gas behaves virtually perfectly.

### TRY IT YOURSELF-4

(1) (B)

(2) (D)

(3) (C)

(4) (B)

(5) (B)

(6) (B)

(7) (C)

(8) (B)

**CHAPTER-5: STATES OF MATTER**

**EXERCISE-1**

- (1) (D). London forces, dipole-dipole forces and dipole-induced dipole forces are included as van der Waals' forces.
- (2) (B). Hydrogen bond is a special case of dipole-dipole interaction. Hydrogen bond is found between the molecules in which highly polar bonds (like HF, OH, N-H) are present.
- (3) (A). Greater the heat of vaporisation, greater are the intermolecular forces.
- (4) (A). Covalent bond and electrostatic forces are not included in the term of intermolecular forces.
- (5) (A). Dipole-dipole interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved e.g., HCl molecules. The attractive force decreases with the increase of distance between the dipoles.
- (6) (A). Force of attraction acts between two temporary dipoles is known as London force. Another name for this force is dispersion force.
- (7) (B). Let the wt. of ethane and H<sub>2</sub> = w gm

$$\therefore \text{No. of moles of } C_2H_6 = \frac{w}{30}$$

$$\text{No. of moles of } H_2 = \frac{w}{2}$$

$$\text{Total no. of moles} = \frac{w}{30} + \frac{w}{2} = \frac{16w}{30}$$

$$\text{Mole fraction of } H_2 = \frac{w}{2} \times \frac{30}{16w} = \frac{15}{16}$$

(8) (B).  $\frac{r_{O_2}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{O_2}}} = \frac{1}{\sqrt{2}}$

- (9) (B). Initial volume (V<sub>1</sub>) = 2.4L,  
Initial pressure (P<sub>1</sub>) = 740 mm.  
Final volume (V<sub>2</sub>) = ?  
Final pressure (P<sub>2</sub>) = 760 mm.  
P<sub>1</sub>V<sub>1</sub> = P<sub>2</sub>V<sub>2</sub> ;

$$\therefore V_2 = \frac{740 \times 2.4}{760} = 2.34 \text{ litres.}$$

- (10) (A). Initial volume (V<sub>1</sub>) = 580 ml,  
T<sub>1</sub> = 17 + 273 = 290 K  
Final Volume (V<sub>2</sub>) = ?  
T<sub>2</sub> = 100 + 273 = 373 K

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \therefore V_2 = T_2 \times \frac{V_1}{T_1} = 373 \times \frac{580}{290} = 746 \text{ ml.}$$

- (11) (D). According to Boyle's law  $V \propto \frac{1}{P}$

$$V = \frac{\text{Constant}}{P}; VP = \text{Constant.}$$

- (12) (A). Mixture of SO<sub>2</sub> and Cl<sub>2</sub> are reacted chemically and

forms SO<sub>2</sub>Cl<sub>2</sub>. That is why mixture of these gases is not applicable for Dalton's law.

- (13) (A). We know that molecular mass of hydrogen M<sub>1</sub> = 2 and that of helium M<sub>2</sub> = 4, we also know that Graham's law of diffusion

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{4}{2}} = \sqrt{2} = 1.4$$

- (14) (D). According to Charles' law  $V \propto T$  i.e., air expands on heating, its density decreases. Hence hot air is lighter.

- (15) (C).  $p \propto T \Rightarrow \frac{p}{T} = \text{constant} = k_3$

This relationship can be derived from Boyle's law and Charles' Law.

- (16) (A). Applying,  $PV = \frac{w}{M}RT$  to both the gases separately

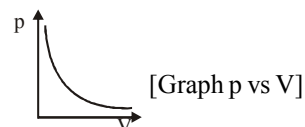
$$P_{O_2} = \frac{4}{32} \times \frac{0.0821 \times 273}{1} = 2.81 \text{ atm}$$

$$P_{H_2} = \frac{2}{2} \times \frac{0.0821 \times 273}{1} = 22.4 \text{ atm}$$

Now, according to Dalton's law,

$$P_{\text{Total}} = P_{O_2} + P_{H_2} = 2.81 + 22.4 = 25.21 \text{ atm.}$$

- (17) (D). From Boyle's law,  $p \propto \frac{1}{V}$



$$pV = \text{constant} \text{ or } p_1V_1 = p_2V_2$$



Graph, pV vs V Graph, pV vs p

- (18) (C). In 1811 Italian scientist Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes which is now called as Avogadro law.

- (19) (C). Boyle's law relates pressure and volume of a gas at constant temperature i.e.,

$$V \propto \frac{1}{P} \text{ (at constant T).}$$

- (20) (A). Given, P = 16 atm, V = 9 litre.  
T = 300 K, M<sub>CH<sub>4</sub></sub> = 16,  
R = 0.08 litre atm/k.

$$PV = \frac{w}{M} \times R \times T$$

$$16 \times 9 = \frac{w}{16} \times 0.08 \times 300; w = 96 \text{ gm.}$$



- (21) (A). The gram molecular weight of  $\text{SO}_2 = 64 \text{ gm/mole}$ .  
Since 1 mole of  $\text{SO}_2$  occupies a volume of 22.4 litres at S.T.P.

$$\text{Density of } \text{SO}_2 = \frac{64}{22.4} = 2.86 \text{ gm/lit.}$$

- (22) (B).  $PV = nRT$ ,  $V = \frac{(5)(0.082)(298)}{2} = 61.09 \text{ litres.}$

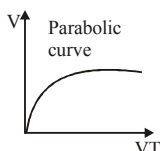
- (23) (A).

(A) From ideal gas equation at constant pressure for fixed mass of gas.

$$V \propto T \Rightarrow V^2 \propto (VT)$$

(B)  $V \propto T$

(C)  $\frac{V}{T} = \text{constant}$



- (24) (C). The value of universal gas constant can be expressed in different units and its value would depend only on the units of the measurement.

- (25) (A).  $P_1 = 760 \text{ mm Hg}$ ,  $V_1 = 600 \text{ mL}$ ,  
 $T_1 = 25 + 273 = 298 \text{ K}$   
 $V_2 = 640 \text{ mL}$  and  $T_2 = 10 + 273 = 283 \text{ K}$   
According to combined gas law

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

$$P_2 = \frac{(760 \text{ mm Hg}) \times (600 \text{ mL}) \times (283 \text{ K})}{(640 \text{ mL}) \times (298 \text{ K})}$$

$$= 676.6 \text{ mm Hg}$$

- (26) (C). Applying  $PV = nRT$ ,  
 $P = 1 \text{ atm}$ ,  $V = 0.224 \text{ L}$ ,  
 $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$ ,  $T = 273 \text{ K}$

$$d = \frac{1 \times 0.224}{0.0821 \times 273} = 0.01$$

- (27) (C). RMS velocity

$$u = \sqrt{\left( \frac{n_1 v_1^2 + n_2 v_2^2 + n_3 v_3^2 + \dots}{n} \right)} = \sqrt{\left( \frac{254}{19} \right)}$$

$$= 3.6 \text{ cm sec}^{-1}$$

- (28) (C). Average velocity ( $v$ ) =  $0.9213 \times \text{RMS velocity (u)}$

$$\text{RMS velocity (u)} = \frac{C}{0.9213} = \frac{45475}{0.9213}$$

$$= 49360 \text{ cm/sec.}$$

- (29) (C).  $\sqrt{\frac{3RT}{32}} = \sqrt{\frac{3 \times R \times 300}{2}}$ ,  $\frac{3RT}{32} = \frac{3R \times 300}{2}$

$$T = \frac{300 \times 32}{2} = 4800 \text{ K.}$$

$$\text{Then in } ^\circ\text{C, } T = 4800 - 273 = 4527^\circ\text{C}$$

- (30) (B).  $E_K$  (For 1 mole) =  $\frac{3}{2} RT = 3741 \text{ Joule.}$

$$8 \text{ gm of methane} = 1/2 \text{ mole of methane}$$

$$\text{Total energy} = \frac{3741}{2} = 1870.5 \text{ Joule.}$$

- (31) (A).  $v_{\text{rms}}$  of  $\text{SO}_2 = \sqrt{\frac{3RT}{M}}$

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 273}{64}} = 3.26 \times 10^4 \text{ cm/sec.}$$

- (32) (A).  $KE = \frac{3}{2} RT = \frac{3}{2} PV$

$$\therefore P = \frac{2}{3} \frac{E}{V} \text{ for unit volume (V = 1); } P = \frac{2}{3} E$$

- (33) (D). All molecules of an ideal gas show random motion. They collide with each other and walls of container during which they lose or gain energy so they may not have same kinetic energy always.

- (34) (C).  $\frac{U_{\text{H}_2}}{U_{\text{O}_2}} = \sqrt{\frac{T_{\text{H}_2}}{M_{\text{H}_2}} \cdot \frac{M_{\text{O}_2}}{T_{\text{O}_2}}} = \sqrt{\frac{50}{2} \cdot \frac{32}{800}} = 1$

- (35) (A).  $V_{\text{rms}} = \sqrt{\frac{3RT}{M}}$   $\therefore V_{\text{rms}} = \sqrt{T}$

$$\text{Given } V_1 = V, T_1 = 300\text{K}, V_2 = 2V, T_2 = ?$$

$$\frac{V_1}{V_2} = \sqrt{\frac{T_1}{T_2}} \quad \left( \frac{V}{2V} \right)^2 = \frac{300}{T_2}$$

$$T_2 = 300 \times 4 = 1200\text{K}$$

- (36) (A). On increasing pressure, the volume decreases and density increases. So molecules get closer to each other hence mean free path also decreases.

- (37) (D). Most probable velocity : mean velocity :

$$V_{\text{rms}} = \sqrt{\frac{2RT}{M}} : \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} = \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

- (38) (B). Molecular weight of  $\text{Cl}_2$  is more than molecular weight of  $\text{N}_2$ .

- (39) (B).  $u_{\text{rms}} > \bar{v}_{\text{avg}} > u_{\text{mp}}$

$$1.225 : 1.128 : 1$$

- (40) (C). Particles of gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the wall of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

- (41) (C). RMS speed is independent of number of molecules,

$$u_{\text{rms}} = \sqrt{\frac{3RT}{M}},$$

where, symbols have their usual meaning.

- (42) (B). Because molecules of real gases have intermolecular forces of attraction so the effective impact on the wall of container is diminished.

- Pressure of real gas is reduced by  $\frac{a}{V^2}$  factor hence behaviour of real gas deviate from ideal behaviour.
- (43) (C).  $M. wt. = V.d. \times 2 = 70 \times 2 = 140$
- $$x = \frac{m.wt.}{wt.of[CO]} = \frac{140}{[12+16]} = 5$$
- (44) (B). At high temperature and low pressure, Vander Waal's equation is reduced to ideal gas equation.  
 $PV = nRT$   
 $PV = RT$  (For 1 mole of gas)
- (45) (B). Compressibility factor,  $(Z) = \frac{PV}{nRT}$
- $$Z = \frac{40 \times 0.4}{1 \times 0.0821 \times 300} = 0.65$$
- Since  $Z < 1$ , hence the gas is more compressible than expected from ideal behaviour.
- (46) (B). The real gases show ideal gas behaviour when pressure approaches zero.
- (47) (B). Pressure correction factor accounts for intermolecular forces.
- (48) (D). For 1 mole of molecules,
- $$b = 4VN_A = 4 \left[ \frac{4}{3} \pi r^3 \right] N_A$$
- (49) (A). Real gas equation is  $\left( P + \frac{a}{V_m^2} \right) (V_m - b) = RT$
- $$PV_m + \frac{a}{V_m} - Pb - \frac{ab}{V_m^2} = RT$$
- As  $P$  is small, thus  $V_m$  will be large and the terms  $Pb$  and  $\frac{ab}{V_m^2}$  can be neglected.
- $$PV_m + \frac{a}{V_m} = RT \text{ or } PV_m = RT - \frac{a}{V_m}$$
- Thus,  $Z = \frac{PV_m}{RT} = 1 - \frac{a}{RTV_m}$
- (50) (C). We know that,  $Z = \frac{V_{(real)}}{V_{(ideal)}}$
- Since  $Z > 1$ , it means  $V_{(real)} > V_{(ideal)}$   
 At STP,  $V_{ideal} = 22.4 \text{ L} = 22.4 \text{ dm}^3$   
 Hence,  $V_{real} > 22.4 \text{ dm}^3$ .
- (51) (C). It can be seen that at constant temperature  $pV$  versus  $p$  plot for ideal gas is a straight line with parallel to the axis which represents pressure.
- (52) (C). Graphs a and b show real gas behaviour because at constant temperature  $pV$  versus  $p$  plot is not a straight line.
- (53) (C). van der Waals constant 'a' gives a measure of intermolecular forces. In case of  $NH_3$ , intermolecular H-bonds exist, that increases the value of 'a'.
- (54) (B). According to the figure,  $H_2$  and He always show positive deviation from the ideal gas behaviour at high pressure. CO and  $CH_4$  show negative deviation then positive deviation from ideal gas with increase of pressure.
- (55) (C). Here, CO and  $CH_4$  show negative as well as positive deviation from the ideal gas behaviour.
- (56) (C). The temperature below which the gas can be liquefied by the application of pressure alone is called critical temperature.
- (57) (C). At above critical temperature, substances are existing in gaseous state, since gas cannot be liquefied above it.
- (58) (D). Due to absence of inter molecular attraction ideal gas cannot be liquefied at any volume of  $P$  and  $T$ .
- (59) (B).  $O_2$  has low critical temperature whereas  $NH_3$  has critical temperature higher than room temperature.
- (60) (D). The relationship between critical constants is
- $$P_c V_c = \frac{3}{8} RT_c$$
- (61) (B). Higher the value of  $T_c$ , more easily the gas can be liquified.
- (62) (B). Both surface tension and viscosity decrease with temperature.
- (63) (C). The normal boiling point of water is  $100^\circ\text{C}$  (373 K) is standard boiling point is  $99.6^\circ\text{C}$  (372.6 K).
- (64) (C).  $P_{dry} = P_{total} - \text{aqueous tension}$
- (65) (C). The viscous force which acts between two layers is directly proportional to area of contact and velocity gradient.  
 $F \propto A$  (where,  $A$  is the area of contact)
- $$F \propto \frac{du}{dz}$$
- (where,
- $\frac{du}{dz}$
- is velocity gradient)
- $$F = A \frac{du}{dz}; F = \eta \cdot A \frac{du}{dz}$$
- $\eta$  is proportionality constant and is called coefficient of viscosity. SI unit of viscosity coefficient is  $\text{Ns m}^{-2}$  or Pascal second.

### EXERCISE-2

(1) (B). Moles of  $H_2 = \frac{1}{2} = 0.5$

Moles of  $N_2 = \frac{1.4}{28} = 0.05$

Total number of moles of gas ( $n$ ) = 0.55  
 Using  $PV = nRT$

$$P = \frac{nRT}{V} = \frac{0.55 \times 0.0821 \times 400}{5} = 3.61 \text{ atm.}$$

(2) (C).  $P_{dry \text{ gas}} = 773 - 13 = 760 \text{ torr} = \frac{760}{760} = 1 \text{ atm}$

$$PV = nRT$$

$$1 \times \frac{171}{1000} = \frac{0.333}{M. wt.} \times 0.0821 \times 288$$

$$M = 46 \text{ g. per mol.}$$

- (3) (A). Partial Pressure = Mole fraction  $\times$  Total pressure  
= Vol. fraction  $\times$  Total pressure

$$P_{O_2} = 0.2 \times 760 = 152 \text{ mm}$$

$$P_{N_2} = 0.8 \times 760 = 608 \text{ mm}$$

- (4) (B).  $p_{N_2} = \text{its mole-fraction} \times P_{\text{total}}$   

$$= \frac{2.8/28}{\frac{2.8}{28} + \frac{2.8}{44} + \frac{4.4}{44}} \times 700 = \frac{0.1}{0.3} \times 700 = 233.3 \text{ Torr.}$$

- (5) (A). Mol. mass  $^{235}\text{UF}_6 = 235 + 6 \times 19 = 349$   
Mol. mass  $^{238}\text{UF}_6 = 238 + 6 \times 19 = 352$

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{352}{349}} = 1.0043$$

$$r_1 : r_2 :: 1.0043 : 1.0000$$

- (6) (C).  $\sqrt{\left(\frac{M_{\text{gas}}}{M_{\text{H}_2}}\right)} = \frac{\text{Rate of diffusion of H}_2}{\text{Rate of diffusion of gas}}$   

$$\sqrt{\left(\frac{M_{\text{gas}}}{2}\right)} = \left(\frac{1}{1/6}\right); M_{\text{gas}} = 2 \times 36 = 72$$

- (7) (B).  $\frac{VD_A}{VD_B} = \frac{M_A}{M_B}; \frac{3}{1} = \frac{M_A}{M_B}$ ,

$$\text{So Mol. wt of A } (M_A) = 3 M_B.$$

- (8) (B).  $K = \frac{3}{2} nRT = \frac{3}{2} \times \frac{8}{16} \times 8.314 \times 300$   

$$= 1869.75 \text{ Joules}$$

- (9) (B). According to Charle's law,

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

$$\frac{3L}{(273+32) \text{ K}} = \frac{V_2}{(273+18) \text{ K}}$$

$$\text{or } V_2 = \frac{3 \times 291}{305} = 2.86 \text{ litres.}$$

- (10) (D).  $PV = nRT$

$$\frac{780}{760} \times 1 = n \times 0.082 \times (273 - 23)$$

$$n = \frac{780}{760 \times 0.082 \times 250} = 0.0501 \text{ moles.}$$

$$0.0501 \text{ moles of the gas weight} = 1.40 \text{ gm.}$$

$$1 \text{ mole of gas weight} = \frac{1.40}{0.0501} = 28 \text{ gram.}$$

So gas is  $N_2$ .

- (11) (C). Given  $V = 6$  litre,  $T = 353$  K,  $R = 0.082$ ,  
 $W = 5$  gm.  $M = 207.3$

$$PV = \frac{W}{M} \times R \times T$$

$$P \times 6 = \frac{5}{207.3} \times 0.082 \times (273 + 80)$$

$$P = \frac{5 \times 0.082 \times 353}{6 \times 207.3} = 0.11 \text{ atm.}$$

- (12) (A). Given  $w_{N_2} = 28$  gm,  $P = 2.46$  atm,  
 $V = 10$  litre,  $M_{N_2} = 28$ ,

$$PV = \left(\frac{w}{M}\right) RT$$

$$2.46 \times 10 = \left(\frac{28}{28}\right) \times 0.0821 \times T; T = 300 \text{ K.}$$

- (13) (A).  $\frac{d_1}{d_2} = \frac{1}{2}; \frac{T_1}{T_2} = \frac{2}{1} \therefore \frac{P_1}{P_2} = \frac{V_2}{V_1} \times \frac{T_1}{T_2} = \frac{T_1 \cdot d_1}{T_2 \cdot d_2}$

$$\frac{P_1}{P_2} = \frac{2}{1} \cdot \frac{1}{2} = \frac{1}{1}$$

- (14) (A). Applying  $P_1 V_1 = P_2 V_2$   
 $P_1 = 730$  mm,  $V_1 = 380$  mL,  
 $P_2 = 760$  mm,  $V_2 = ?$

$$V_2 = \frac{730 \times 380}{760} = 365 \text{ mL.}$$

- (15) (B). Applying  $P_1 V_1 = P_2 V_2$   
 $P_1 = 9.962 \times 10^4 \text{ Nm}^{-2}$ ,  $V_1 = 95 \text{ cm}^3$   
 $P_2 = 10.13 \times 10^4 \text{ Nm}^{-2}$ ,  $V_2 = ?$

$$V_2 = \frac{9.962 \times 10^4 \times 95}{10.13 \times 10^4} = 93.4 \text{ cm}^3$$

- (16) (D). At temperature  $27^\circ\text{C}$  (300 K)

$$\text{RMS, } u_1 = \sqrt{\frac{3R \times 300}{M}}$$

At temperature  $927^\circ\text{C}$  (1200 K)

$$\text{RMS, } u_2 = \sqrt{\frac{3R \times 1200}{M}}$$

$$= \sqrt{\frac{3R \times 4 \times 300}{M}} = 2 \sqrt{\frac{3R \times 300}{M}} = 2u_1$$

Thus, RMS speed gets doubled.

- (17) (C). According to Charle's law  
 $V \propto T$  at constant P

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}; V_1 = 22.4 \text{ L, } T_1 = 273 \text{ K}$$

$$T_2 = 373 \text{ K, } V_2 = ?$$

$$V_2 = \frac{T_2}{T_1} \times V_1 = \frac{373}{273} \times 22.4 = 30.6 \text{ L}$$

Thus graph (C) is correct.

- (18) (A). At moderate pressure, volume  $V$  decreases, so that,  $a/V^2$  cannot be neglected.

However,  $b$  can be neglected in comparison to  $V$ . Thus, van der Waals equation reduces to

$$\left(P + \frac{a}{V^2}\right)V = RT \text{ or } PV + \frac{a}{V} = RT \Rightarrow PV = RT - \frac{a}{V} \quad (24)$$

$$\text{or } \frac{PV}{RT} = 1 - \frac{a}{RTV} \text{ i.e., } Z = 1 - \frac{a}{RTV}$$

Therefore, compressibility factor is less than one at moderate pressure and increases with increase of temperature.

- (19) (D). Applying,  $PV = nRT$  for dry gas

$$P = ?, V = 428 \text{ mL} = 0.428 \text{ L,}$$

$$n = 0.0168 \text{ mol}$$

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

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

$$P = \frac{0.0168 \times 0.0821 \times 298}{0.428} = 0.96 \text{ atm}$$

$$= (0.96 \times 760) \text{ mm} \approx 730 \text{ mm}$$

$$P_{\text{moist gas}} = P_{\text{dry gas}} + P_{\text{water vapour}}$$

$$P_{\text{water vapour}} = 754 - 730 = 24 \text{ mm Hg.}$$

- (20) (C).  $KE = \frac{3}{2}nRT = \frac{3}{2} \times 2 \times 8.314 \times 300$

$$(T = 27^\circ\text{C} = (273 + 27) \text{ K} = 300 \text{ K})$$

$$\therefore \text{K.E.} = 7482.6 \text{ J.}$$

- (21) (D). Applying,  $PV = \frac{m}{M}RT$

$$V = 600 \text{ mL} = 0.6 \text{ L; } m = 22 \text{ g; } M = 44 \text{ u}$$

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

$$P = \frac{22}{44} \times \frac{0.0821 \times 298}{0.6} = 20.4 \text{ atm}$$

This pressure is developed by dry ice.

Final pressure inside the vessel

$$= P + \text{atmospheric pressure}$$

$$= 20.4 + 1 = 21.4 \text{ atm.}$$

- (22) (B).  $u_{N_2} = \sqrt{\frac{3RT}{M}}$

Mass of nitrogen atom

$$= \frac{\text{Mass of nitrogen molecule}}{2} = \frac{M}{2}$$

$$u_{N_2} = \sqrt{\frac{3R(2T)}{M/2}} = 2\sqrt{\frac{3RT}{M}} = 2u_{N_2}$$

- (23) (D). Moles of  $O_2 = \frac{70.6 \text{ g}}{32 \text{ g mol}^{-1}} = 2.21 \text{ mol}$

$$\text{Moles of Ne} = \frac{167.5 \text{ g}}{20 \text{ g mol}^{-1}} = 8.375 \text{ mol}$$

Mole fraction of

$$O_2 = \frac{2.21}{2.21 + 8.375} = 0.21$$

$$\text{Mole fraction of Ne} = 1 - 0.21 = 0.79$$

Partial pressure of a gas

$$= \text{Mole fraction} \times \text{total pressure}$$

$$\text{Partial pressure of } O_2 = 0.21 \times 25 = 5.25 \text{ bar.}$$

$$\text{Partial pressure of Ne} = 0.79 \times 25 = 19.75 \text{ bar}$$

- (25) (B). From Boyle's law

$$P_1 = 1 \text{ bar, } P_2 = ?, V_1 = 2 \text{ L, } V_2 = 1 \text{ L}$$

$$P_1V_1 = P_2V_2$$

$$1 \times 2 = p_2 \times 1 ; P_2 = 2 \text{ bar}$$

- (25) (C). We know that  $d = \frac{PM}{RT}$

$$\text{i.e., } d \propto P \text{ and } d \propto 1/T$$

Hence density is maximum at high pressure and low temperature.

- (26) (C).  $Z > 1$  shows that it is difficult to compress the gas as compared to ideal gas.

- (27) (A). With increase in temperature, most probable speed increases but the fraction possessing this speed decreases.

- (28) (D). Density of air = 0.00130 g/ml = 1.3 g/L

$$\text{We know, } PM = dRT$$

$$M = \frac{dRT}{P}$$

At standard state,

$$M = \frac{1.3 \times 0.0821 \times 273}{1} = 29.14$$

$$M = 2 \times \text{vapour density}$$

$$\therefore \text{Vapour density} = \frac{29.14}{2} = 14.57$$

- (29) (C). Charles' law :

For given gas at constant pressure  $V \propto T$

- (30) (B). Isobar.

- (31) (A). Order of pressure:  $p_1 < p_2 < p_3 < p_4$

- (32) (A). Number of moles originally present =  $\frac{2.24}{22.4} = 0.1$

After leakage,  $PV = nRT$

$$\text{or } n = \frac{PV}{RT} = \frac{(570/760)(2.24)}{0.0821 \times 273} = 0.075$$

Hence, no. of moles leaked out

$$= 0.1 - 0.075 = 0.025 \text{ mole.}$$

- (33) (B).  $u_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}}$

$$\text{But } \frac{V}{M} = \frac{1}{\text{density (d)}}$$

$$u_{\text{rms}} = \sqrt{\frac{3P}{d}} = \sqrt{\frac{3 \times 100 \times 10^3}{0.1}} = 1732 \text{ m/s}$$

- (34) (C). We know,  $PM = dRT$

$$P = 2 \text{ atm, } M_{\text{CH}_4} = 16$$

$$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$T = 27^\circ\text{C} = 300 \text{ K}$$

$$d = \frac{2 \times 16}{0.0821 \times 300} = 1.3 \text{ g/L}$$

- (35) (B). Equal number of molecules means equal number of moles i.e., equal mole fraction since partial pressure  $\propto$  mole fraction.

$$p_{N_2} : p_{O_2} \text{ or } p_{O_2} = \frac{650}{2} \text{ mm}$$

- (36) (B).  $v_{av} = \sqrt{\frac{8RT}{\pi M}}$  ;  $v_{av} \propto \sqrt{T}$

$$\frac{2}{v_0} = \sqrt{\frac{300}{1200}} = \sqrt{\frac{1}{4}} = \frac{1}{2} ; v_2 = 4 \text{ m/s}$$

- (37) (A). Applying,  $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$V_1 = 1 \text{ L}, T_1 = 25 + 273 = 298 \text{ K}$$

$$V_2 = ?, T_2 = 35 + 273 = 308 \text{ K}$$

$$V_2 = \frac{1}{298} \times 308 = 1.033 \text{ L}$$

$$\text{Capacity of flask} = 1 \text{ L}$$

$$\text{Volume of air escaped} = 1.033 - 1 = 0.033 \text{ L} = 33 \text{ mL.}$$

- (38) (A).  $Z = \frac{PV}{nRT}$

$$\text{At STP, } P = 1 \text{ atm, } T = 273 \text{ K}$$

$$\text{Given, } V = 50 \text{ L, } n = 2 \text{ moles}$$

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

$$Z = \frac{1 \times 50}{2 \times 0.0821 \times 273} = 1.1$$

Since  $Z > 1$ , the gas shows positive deviation from ideal behaviour.

- (39) (B). As  $P$  and  $V$  remains constant,  $n_1 T_1 = n_2 T_2$

$$n_1 = \frac{0.4}{4} = 0.1, T_1 = T \text{ K,}$$

$$n_2 = \frac{0.40 - 0.08}{4} = 0.08$$

$$T_2 = (T + 50) \text{ K.}$$

$$\text{On putting the values, } 0.1 \times T = 0.08 \times (T + 50)$$

$$0.1T = 0.08T + 4 \text{ } \Rightarrow 0.1T - 0.08T = 4$$

$$0.02T = 4 \text{ } \Rightarrow T = 200 \text{ K}$$

- (40) (C). Draw a line at constant pressure parallel to volume-axis. Take volume corresponding to each temperature.

$$\text{From volume axis, } V_1 > V_2 > V_3$$

$$\text{Hence } T_1 > T_2 > T_3.$$

### EXERCISE-3

- (1) 4.  $U_{rms}$  at temp  $T_1 = \sqrt{\frac{3RT_1}{M}}$ ,

$$U_{rms} \text{ at temp } T_2 = \sqrt{\frac{3RT_2}{M}}$$

$$\therefore \frac{U_{rms} \text{ at temp. } T_2}{U_{rms} \text{ at temp. } T_1} = \sqrt{\frac{T_2}{T_1}}$$

$$\text{or } \frac{10 \times 10^4}{5 \times 10^4} = \sqrt{\frac{T_2}{T_1}} \text{ or } \sqrt{\frac{T_2}{T_1}} = \frac{4}{1}$$

$\therefore$  Temperature is to be increased 4 times.

- (2) 3. My weight =  $80 \times 10^3 \text{ gm}$

$$\text{Wt. of hydrogen in each balloon} = 50 \times 2 \text{ gm}$$

$$\text{volume of each balloon} = \frac{50 \times 0.082 \times 300}{0.05} = 24600 \text{ lit.}$$

Hence volume of displaced air by each balloon = 24600 lit.

Let  $x$  no. of such balloons are required

$$\therefore 80 \times 10^3 + x \times 50 \times 2 = 24600 \times 1.25 \times x$$

$$\text{or } 80 \times 10^3 = 30650x \text{ or } x = 2.610$$

$\therefore$  To fly in the sky I must attach 3 such type of balloons should attach with my self.

- (3) 1. The first step is to calculate the number of moles of each

$$\text{gas using the ideal gas law in the form : } n = \frac{PV}{RT}$$

$$n_{O_2} = \frac{(1.0 \text{ atm}) (46\text{L})}{(0.08206 \text{ L atm / K mol}) (298\text{K})} = 1.9 \text{ mol}$$

$$n_{He} = \frac{(1.0 \text{ atm}) (12\text{L})}{(0.08206 \text{ L atm / K mol}) (298\text{K})} = 0.49 \text{ mol}$$

The tank containing the mixture has a volume of 5.0L, and the temperature is 25°C. We can use these data and the ideal gas law to calculate the partial pressure of each gas :

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

$$P_{O_2} = \frac{(1.9 \text{ mol}) (0.08206 \text{ L atm / K mol}) (298\text{K})}{5.0 \text{ L}} = 9.3 \text{ atm}$$

$$P_{He} = \frac{(0.49 \text{ mol}) (0.08206 \text{ L atm / K mol}) (298\text{K})}{5.0 \text{ L}} = 2.4 \text{ atm}$$

The total pressure is the sum of the partial pressures :

$$P_{\text{total}} = P_{O_2} + P_{He} = 9.3 \text{ atm} + 2.4 \text{ atm} = 11.7 \text{ atm}$$

- (4) 3. First we calculate the number of moles of  $\text{CO}_2$  consumed in the reaction. The drop in pressure, which is

$7.9 \times 10^{-3} \text{ atm} - 1.2 \times 10^{-4} \text{ atm}$ , or  $7.8 \times 10^{-3} \text{ atm}$ , corresponds to the consumption of  $\text{CO}_2$ . Using the ideal gas equation, we write

$$n = \frac{PV}{RT} = \frac{(7.8 \times 10^{-3} \text{ atm}) (2.4 \times 10^5 \text{ L})}{(0.0821 \text{ L.atm / K.mol}) (312\text{K})} = 73 \text{ mol}$$

From the equation we see that 1 mole  $\text{CO}_2 = 1 \text{ mol Li}_2\text{CO}_3$ , so the amount of  $\text{Li}_2\text{CO}_3$  formed is also 73 moles. Then, with the molar mass of  $\text{Li}_2\text{CO}_3$  (73.89g) we calculate its mass :

$$\begin{aligned} \text{mass of Li}_2\text{CO}_3 \text{ formed} &= 73 \text{ mol Li}_2\text{CO}_3 \times \frac{73.89 \text{ g Li}_2\text{CO}_3}{1 \text{ mol Li}_2\text{CO}_3} \\ &= 5.4 \times 10^3 \text{ g Li}_2\text{CO}_3 \end{aligned}$$

- (5) 6.  $P = 11.0 \text{ atm}$ ,  $b = 0.05 \text{ L mol}^{-1}$ ,  $V = 4 \text{ L}$ ,  
 $T = 300 \text{ K}$ ,  $n = 2$ ,  $a = ?$

Using van der Waal's equation,  $\frac{a}{V^2} + \frac{an^2}{V^2} (V - nb) = nRT$

$$\frac{a}{(4)^2} + \frac{4a}{(4)^2} (4 - 2 \times 0.05) = 2 \times 0.0821 \times 300$$

On solving,  $a = 6.523 \text{ atm L}^2 \text{ mol}^{-2}$

- (6) 9. Recognized that 1 mole of an ideal gas occupies 22.41L at STP, we write

$$V = 7.40 \text{ g NH}_3 \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3} \times \frac{22.41 \text{ L}}{1 \text{ mol NH}_3} = 9.74 \text{ L}$$

Because 7.40g is smaller than the molar mass of  $\text{NH}_3$  (17.03g), we would expect the volume to be smaller than 22.41L at STP. Therefore, the answer is reasonable. The problem can be solved in a different way by first converting 7.40g of  $\text{NH}_3$  to number of moles of  $\text{NH}_3$  and then applying the ideal gas equation.

- (7) 6. Let the unknown compound of Xe and F be  $\text{XeF}_n$  (A). The ratio of rate of diffusion of  $\text{N}_2$  to that of (A) is given as

$$\frac{r_{\text{N}_2}}{r_A} = \frac{0.8}{1.6} \sqrt{\frac{M_A}{28}}; \frac{1}{38} \sqrt{\frac{56.2}{1}} = \frac{1}{2} \sqrt{\frac{M_A}{28}} \therefore M_A = 245$$

The molecular mass of A =  $131 + 19n = 245 \Rightarrow n = 6$

$\therefore$  molecular formula of the compound A is  $\text{XeF}_6$ .

- (8) 2. We can solve this problem using Boyle's law,  $PV = k$  which can also be written as

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

where the subscripts 1 and 2 represent two states (conditions) of the gas (both at the same temperature).

In this case

$$P_1 = 5.6 \times 10^3 \text{ Pa}, P_2 = 1.5 \times 10^4 \text{ Pa}$$

$$V_1 = 1.53 \text{ L}, V_2 = ?$$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{5.6 \times 10^3 \text{ Pa} \times 1.53 \text{ L}}{1.5 \times 10^4 \text{ Pa}} = 0.57 \text{ L}$$

The new volume will be 0.57 L

- (9) 3. Let the molecular masses of A and B be  $M_A$  and  $M_B$  respectively. Pressure exerted by the gas B =  $(1.5 - 1.0) = 0.5 \text{ atm}$ , volume and temperature are same in both the gases.

For gas A,  $P = 1 \text{ atm}$ ,  $m = 2 \text{ g}$ .

$$\text{We know } PV = \frac{m}{M}RT$$

$$\therefore M_A = \frac{m}{PV}RT = \frac{2RT}{V} \dots\dots\dots (1)$$

For gas B,  $P = 0.5 \text{ atm}$ ,  $m = 3 \text{ g}$

$$M_B = \frac{3RT}{0.5 \times V} \dots\dots\dots (2)$$

Dividing equation (1) by equation (2)

$$\frac{M_A}{M_B} = \frac{2RT}{V} \times \frac{0.5V}{3RT} = \frac{1}{3}. \text{ Thus } M_A : M_B = 1 : 3$$

- (10) 6. The problem requires two steps. First, we calculate the number of moles of  $\text{N}_2$  generated from the decomposition of 60.0g of  $\text{NaN}_3$ . Next we calculate the volume of the  $\text{N}_2$  gas at the given temperature and pressure.

Moles of  $\text{N}_2$

$$= 60.0 \text{ g NaN}_3 \times \frac{1 \text{ mol NaN}_3}{65.02 \text{ g NaN}_3} \times \frac{3 \text{ mol N}_2}{2 \text{ mol NaN}_3} = 1.38 \text{ mol}$$

$\text{N}_2$

The volume of 1.38 moles of  $\text{N}_2$  can be obtained by using the ideal gas equation :

$$V = \frac{nRT}{P} = \frac{(1.38 \text{ mol})(0.0821 \text{ L atm / K.mol})(80 + 273) \text{ K}}{(823 / 760) \text{ atm}} = 36.9 \text{ L}$$

- (11) 5. To solve this problem we take the ideal gas law and segregate the changing variables and the constants on opposite sides of the equation. In this case volume and temperature change, and number of moles and pressure (and of course R) remain constant.

Thus  $PV = nRT$  becomes

$$\frac{V}{T} = \frac{nR}{P} \text{ which leads to } \frac{V_1}{T_1} = \frac{nR}{P} \text{ and } \frac{V_2}{T_2} = \frac{nR}{P}$$

Combining these gives

$$\frac{V_1}{T_1} = \frac{nR}{P} = \frac{V_2}{T_2} \text{ or } \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

We are given  $T_1 = 5^\circ\text{C} + 273 = 278 \text{ K}$

$$T_2 = 86^\circ\text{C} + 273 = 359 \text{ K}$$

$$V_1 = 3.8 \text{ L}, V_2 = ?$$

$$\text{Thus, } V_2 = \frac{T_2V_1}{T_1} = \frac{(359\text{K})(3.8\text{L})}{278\text{K}} = 4.9\text{L}$$

- (12) 600.

**EXERCISE-4**

- (1) (A).  $PV = nRT$  or  $n = \frac{PV}{RT}$
- For  $V = 1$  lit., so  $n = \frac{P}{RT}$
- (2)  $R = 8.314 \times 10^7 \text{ erg} - \text{K}^{-1} \text{ mol}^{-1}$
- (3) (A). According to kinetic theory of gases, in an ideal gas between two successive collision a gas molecules travel in a straight line path.

(4) (C).  $\frac{(\text{K.E.})_{40}}{(\text{K.E.})_{20}} = \frac{\frac{3}{2} \times nR \times 313}{\frac{3}{2} \times nR \times 293}$

or  $(\text{K.E.})_{40} = (\text{K.E.})_{20} \times \frac{313}{293}$

- (5) (C). The vander walls constant,  $b$  is a measure of the effective volume occupied by the gas molecules. It is also called as "co-volume or excluded volume".
- (6) (A). It is found that the fraction of molecule with the most probable speed decreases.
- (7) (C). If masses of oxygen and methane are same, then their molar ratio is 1 : 2.  
So, pressure of oxygen = 1/3

(8) (D).  $n = \frac{PV}{RT} = 128 \times 10^{-5} \text{ moles}$

$$= \frac{3170 \times 10^{-5} \text{ atm} \times 1\text{L}}{0.0821 \text{ L atm k}^{-1} \text{ mol}^{-1} \times 300\text{K}} = 1.27 \times 10^{-3} \text{ mol}$$

(9) (D).

	a	b
$\text{Cl}_2$	$6.579 \text{ L}^2 \text{ bar mol}^{-2}$	$0.05622 \text{ L mol}^{-1}$
$\text{C}_2\text{H}_6$	$5.562 \text{ L}^2 \text{ bar mol}^{-2}$	$0.06380 \text{ L mol}^{-1}$

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

At high pressure  $\frac{a}{V^2}$  can be neglected.

$PV - Pb = RT$  ;  $PV = RT + Pb$

$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$  ;  $Z = 1 + \frac{Pb}{RT}$  ;  $Z > 1$  at high pressure.

(11) (C).  $C^* = \text{most probable speed} = \sqrt{\frac{2RT}{M}}$

$\bar{C} = \text{average speed} = \sqrt{\frac{8RT}{\pi M}}$

$C = \text{Mean square speed corrected as rms} = \sqrt{\frac{3RT}{M}}$

$C^* < \bar{C} < C$

$C^* : \bar{C} : C = 1 : \sqrt{\frac{4}{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1.128 : 1.225$

**Note :** As no option correspond to mean square speed, it is understood as misprint. It should be root means square speed . So, Ans is (C).

(12) (D).  $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

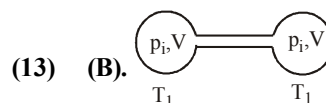
For 1 mole,  $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2}$

At low pressure, terms  $Pb$  &  $\frac{ab}{V^2}$  will be negligible as compared to  $RT$ .

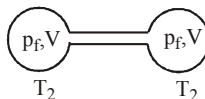
So,  $PV = RT - \frac{a}{V}$

$Z = 1 - \frac{a}{RTV}$



Number of mol of gases in each container =  $\frac{p_i V}{RT_1}$

Total mol of gases in both containers =  $2 \frac{p_i V}{RT_1}$

In left chamber  $n_1 = \frac{p_f V}{RT_1}$  

In right chamber,  $n_2 = \frac{p_f V}{RT_2}$

Total moles of gases should remain constant

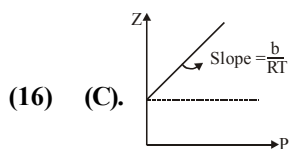
$\frac{2p_i V}{RT_1} = \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2} \Rightarrow p_f = 2p_i \left( \frac{T_2}{T_1 + T_2} \right)$

(14) (C).  $n_T = (0.5 + x)$   
 $PV = n \times R \times T$   
 $200 \times 10 = (0.5 + x) \times R \times 1000$   
 $2 = (0.5 + x) R$   
 $\frac{2}{R} = \frac{1}{2} + x \Rightarrow \frac{4}{R} - 1 = 2x \Rightarrow \frac{4 - R}{2R} = x$

(15) (A).  $T_c = \frac{8a}{27Rb}$ ; Greater value of  $\frac{a}{b} \Rightarrow$  Higher is  $T_c$

Gas	Ar	Ne	Kr	Xe
$\frac{a}{b}$	$\frac{1.3}{3.2}$	$\frac{0.2}{1.7}$	$\frac{5.1}{1}$	$\frac{4.1}{5}$
	= 0.406	= 0.118	= 5.1	= 0.82

$\therefore T_c$  has order : Kr > Xe > Ar > Ne



As  $b \uparrow \Rightarrow$  slope  $\uparrow$

Hence, Xe, will have highest slope.

- (17) (C).
- Gas A and C have same value of 'b' but different value of 'a' so gas having higher value of 'a' have more force of attraction so molecules will be more closer hence occupy less volume.
  - Gas B and D have same value of 'a' but different value of 'b' so gas having lesser value of 'b' will be more compressible.

(18) (D).

(19) (A).  $V_{rms} > V_{avg} > V_{mp}$

(20) (C). Ethyl acetate is polar molecule so dipole-dipole interaction will be present there.

### EXERCISE-5

(1) (C). Due to intermolecular H-bonding the surface tension of  $H_2O$  is more than other liquid. One  $H_2O$  molecule is joined with 4 another  $H_2O$  molecule through H-bond.

(2) (D). Average K.E. =  $\frac{3}{2} RT$

At constant temperature K.E. remains constant

(3) (D). Volume of one water molecules is

$$\frac{18 \text{ cm}^3}{6.023 \times 10^{23}} = 3.0 \times 10^{-23} \text{ cm}^3$$

(4) (D). K.E per atom =  $\frac{(4.4 \times 10^{-19}) - (4.0 \times 10^{-19})}{2}$   
 $= \frac{0.4 \times 10^{-19}}{2} = 2.0 \times 10^{-20}$

(5) (C). Given, mass of  $CH_4$ ,  $w = 6$  g  
 Volume of  $CH_4$ ,  $V = 0.03 \text{ m}^3$   
 $T = 129^\circ\text{C} = 129 + 273 = 402 \text{ K}$   
 $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$   
 Molecular mass of  $CH_4$ ,  
 $M = 12.01 + 4 \times 1.01 = 16.05$

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

$$\therefore P = \frac{w RT}{M V} = \frac{6}{16.05} \times \frac{8.314 \times 402}{0.03}$$

$$= 41647.7 \text{ Pa} \approx 41648 \text{ Pa}$$

(6) (A). Average speed =  $\sqrt{\frac{8RT}{\pi M}}$

If temperature is double, average speed becomes  $\sqrt{2}$  (= 1.41) times.

(7) (C).  $\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \Rightarrow \frac{v_A}{t_A} \times \frac{t_B}{v_B} = \sqrt{\frac{M_B}{M_A}}$

$$\frac{10}{20} = \sqrt{\frac{M_B}{49}} \Rightarrow \frac{1}{4} = \frac{M_B}{49} \therefore M_B = 49/4 = 12.25$$

(8) (B).  $n_{CO} = n_{N_2} \therefore P_{CO} = P_{N_2}$

$$P_{CO} + P_{N_2} = 1 \text{ atm,}$$

$$2P_{N_2} = 1 \text{ atm, } P_{N_2} = 0.5 \text{ atm}$$

(9) (A).  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ ;  $\frac{1.5 \times V}{288} = \frac{1 \times V_2}{298}$

$V_2 = 1.55 V$  i.e. volume of bubble will be almost 1.6 time to initial volume of bubble.

(10) (D).  $\frac{V_A / t_A}{V_B / t_B} = \sqrt{\frac{M_B}{M_A}}$

$$\Rightarrow \frac{150}{200} = \sqrt{\frac{36}{M_A}} \Rightarrow \frac{3}{4} = \sqrt{\frac{36}{M_A}} \Rightarrow \frac{9}{16} = \frac{36}{M_A} \Rightarrow M_A = 64$$



$$(11) \quad (B). \quad r \propto \sqrt{\frac{1}{M}}; \quad \frac{r_2}{r_1} \propto \sqrt{\frac{M_2}{M_1}}; \quad \frac{V_g}{V_{He}} = \sqrt{\frac{4}{M}}$$

$$\frac{1}{9} = \frac{4}{M}; \quad M = 36 \text{ g/mole}$$

(12) (C).

Gas	H <sub>2</sub>	He	O <sub>2</sub>	CO <sub>2</sub>
Value of b	0.0273	0.0318	0.0273	0.0427

Gas	CH <sub>4</sub>	O <sub>2</sub>	H <sub>2</sub>
Value of a	2.25	1.36	0.244

(I) Order of a : CH<sub>4</sub> > O<sub>2</sub> > H<sub>2</sub>

(II) Order of b : H<sub>2</sub> < He < O<sub>2</sub> < CO<sub>2</sub>

(13) (A). Easily liquifiable gases like NH<sub>3</sub>, SO<sub>2</sub> etc. exhibit maximum deviation from ideal gas as for then Z < 1.

CH<sub>4</sub> also exhibits deviation but it is less as compared to NH<sub>3</sub>.

(14) (D). Dipole - induced dipole occurs between polar & Non-polar molecule

HCl	He
Polar	Non-polar
≠ 0	μ = 0

H<sub>2</sub>O and alcohol both are polar molecules.

Cl<sub>2</sub> and CCl<sub>4</sub> both are non-polar molecules.

(15) (C). Real gases show ideal gas behaviour at high temperatures and low pressures.

$$(16) \quad (A). \quad \frac{n_{O_2}}{n_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} \Rightarrow \frac{n_{O_2}}{0.5} = \sqrt{\frac{2}{32}} \quad \therefore n_{O_2} = \frac{1}{8}$$

(17) (C). van der waal constant 'a', signifies intermolecular forces of attraction.

Higher is the value of 'a', easier will be the liquefaction of gas.

$$(18) \quad (D). \quad \text{In real gas equation, } \left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT$$

van der Waal's constant, 'a' signifies intermolecular forces of attraction.

$$(19) \quad (C). \quad \text{Compressibility factor } (Z) = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

$$V_{\text{real}} < V_{\text{ideal}}; \quad \text{Hence } Z < 1$$

If Z < 1, attractive forces are dominant among gaseous molecules and liquefaction of gas will be easy.