UNIT 2

States of Matter

SYLLABUS

Gaseous state : *Measurable properties, the gas laws, Ideal gas equation, kinetic molecular theory, deviation of real gases from ideal behaviour, liquefaction of gases, critical temperature and its importance.*

Liquid state : *Properties of liquids, qualitative description of vapour pressure, surface tension, viscosity.*

Solid state : *Classification of solids based on different binding forces.*

2.1. General Introduction

In Unit I, Section III, we discussed the chemical classification of matter into elements, compounds and mixtures. A passing reference was made about the physical classification of matter into solids, liquids and gases which are called the three states of matter.

The aim of this unit is to discuss some important aspects of each of the three states of matter one by one. However, before we proceed to discuss each of the states, let us try to review what we mean by a solid, a liquid and a gas and in what important characteristic properties the three states differ from each other.

A substance is said to be solid if its melting point is above room temperature under atmospheric pressure ; a liquid if its melting point is below room temperature and boiling point is above room temperature and a gas if its boiling point is below room temperature under atmospheric pressure.

It has been found that in most cases, a given substance can be made to exist in any one of the three states under different conditions of temperature and pressure. For example, water which is a liquid under ordinary conditions of temperature and pressure, can be converted into steam (gas) at 100°C and under one atmosphere or into ice (solid) by cooling to 0°C under one atmosphere pressure.

A given substance can also exist simultaneously in all the three states under certain specified conditions of temperature and pressure. For example, water exists in all the three phases, viz. ice (solid), water (liquid) and water vapours (gas) simultaneously at $0 \cdot 01$°C ($273 \cdot 16$ K) and $4 \cdot 58$ mm pressure.

The temperature at which all the three phases exist together is called triple point.

The change of state is often accompanied by either absorption or evolution of heat. For example, a solid can be converted into a liquid or a liquid into a gas by absorption of heat. This implies that a substance possesses least energy in the solid state but maximum in the gaseous state.

The essential points of difference between the three states of matter, namely, solids, liquids and gases are given in Table 2.1.

TABLE 2.1. Comparison of the characteristics of a solid, a liquid and a gas

SOLID	LIQUID	GAS
1. Molecules are closely packed	Molecules are less closely packed.	Molecules are sufficiently apart from one another.
2. Mutual forces of attraction are the strongest.	Mutual forces of attraction are weaker than those in solids.	Mutual forces of attraction are almost negligible.
3. The density of solids is high.	The density of liquids is lower than that of solids but is much higher than that of gases.	Gases generally have low densities.
4. The positions of molecules in the crystal lattice are fixed and hence solids do not have translatory or rotatory motion but only possess vibratory motion.	Molecules of a liquid have greater freedom of movement. They have some translatory and rotatory motions in addition to the vibratory motion.	Molecules of a gas have large rotatory, vibratory and translatory motions.
5. Molecules of a solid possess least energy.	Molecules of a liquid have higher energies than those of solids.	Gas molecules are most energetic.
6. Solids have both a definite shape and a definite volume.	Liquids do not have definite shapes but have definite volumes.	Gases have neither definite shapes nor definite volumes.
7. Solids possess least compressibility and thermal expansion.	Liquids have slightly higher compressibility and thermal expansion than those of solids.	Gases possess high compressibility and thermal expansion.

Based on the most easily observable characteristic (viz no. 6 in the Table above), solid, liquid and gas may be defined as follows :–

Solid *is defined as that state of matter which possesses a definite shape and a definite volume.* **Liquid** *is defined as that state of matter which has a definite volume but no definite shape. They take up the shape of the vessel in which they are put.* **Gas** *is defined as that state of matter which has neither definite shape nor definite volume.*

Two More States of Matter. Besides the above three states of matter, two more states of matter have been found to exist and discovered recently. One of these (*fourth state*) is called **plasma state** which consists of a mixture of electrons and positively charged ions formed due to superheating of the gaseous state *e.g.* in the sun or stars. Another state (*fifth state*) consists of a supercooled solid in which the atoms lose their individual identity and condense to form a single super atom.

2.2. Intermolecular Forces Versus Thermal Energy

Whether a substance will exist as a solid or a liquid or a gas is the result of competition between :

(*i*) *intermolecular forces i.e.* the forces of interaction between the molecules of that substance which try to bring the molecules closer, and

(*ii*) *thermal energy* possessed by the molecules due to temperature which results into the movement of the molecules and hence tries to kep them apart.

In gases, the intermolecular forces of attraction are weakest while thermal energy is highest (mainfested as random translatory motion of molecules). In solids, intermolecular forces of attraction are strongest while thermal energy is minimum (only due to vibratory motion about the mean position of constituent particles and no translatory motion at all). In liquids, the two types of energies are intermediate between those of gases and solids.

$$\underset{\xrightarrow[\text{Thermal Energy}]{\hspace{10em}}}{\overset{\xleftarrow{\text{Molecular Interaction Energy}}}{\text{Solid} \longrightarrow \text{Liquid} \longrightarrow \text{Gas}}}$$

Some of the properties of solids, liquids and gases can be explained on the basis of their interaction energy and thermal energy as follows :

(*i*) A solid has rigidity because thermal motion is too weak to overpower the strong intermolecular forces of attraction. In a gas, thermal energy is so high that the molecules cannot come close together. Hence there are large empty spaces between them. In a liquid, there is a reasonable balance between the attractive intermolecular forces and thermal energy. Hence molecules in a liquid exist together *i.e.* it is a condensed state of matter but there is no rigidity. That is why they have no definite shape.

(*ii*) A solid melts on heating because on heating, the thermal motion increases.

(*iii*) In both liquids and solid, their molecules exist together *i.e.* both of them are *condensed state of matter* having sufficiently strong intermolecular forces of attraction. Hence they exhibit very low compressibility. On the other hand in gases, there are large empty spaces between the molecules, therefore they possess high compressibility.

SECTION—I

THE GASEOUS STATE

In addition to the various properties of gases listed in the table above, gases obey certain laws, called 'Gas laws'. These laws give quantitative relationships between mass, volume, pressure and temperature of the gas. The aim of the present section is, therefore, first to discuss the measurement of these properties of a gas and then to discuss some of the gas laws obeyed by the gases.

2.3. Measurement of Mass, Volume, Pressure and Temperature

(1) Measurement of Mass. The mass of a gas can be easily determined by weighing the container containing the gas, and then emptying the container by taking out the gas and weighing the empty container again. The difference between the two masses gives the mass of the gas. The amount of the gas is usually expressed in terms of moles which can be obtained by dividing the mass of the gas by its molar mass *i.e.*

$$\boxed{\text{Number of moles} = \frac{\text{Mass in grams}}{\text{Molar mass}}}$$

The moles can be converted into the number of molecules using the relationship

$$1 \text{ mole} = 6.022 \times 10^{23} \text{ molecules}$$

(2) Measurement of Volume. As a gas fills the whole of the vessel in which it is put, hence the volume of the gas is equal to the volume of its container which in turn can be calculated from the dimensions of the container.

The SI unit of volume is m^3. But this is too big a unit. Hence the units commonly employed are cm^3 or dm^3. However the units ml and litres also continue to be used, generally in expressing the volumes of liquids and solutions. These units are inter-related as follows :

$$\boxed{\begin{gathered} 1 \text{ m}^3 = 10^3 \text{ dm}^3 = 10^6 \text{ cm}^3 \\ 1 \text{ ml} = 1 \text{ cm}^3 \\ 1 \text{ litre} = 10^3 \text{ cm}^3 = 1 \text{ dm}^3 = 10^{-3}\, m^3 \end{gathered}}$$

(3) Measurement of Pressure. The instrument used for the measurement of atmospheric pressure is called a **barometer.** The principle of a barometer is illustrated in Fig. 2.1 (a). It consists in inverting a tube filled with mercury in a dish of mercury. The height of the mercury column above the level of mercury in the dish is a measure of the atmospheric pressure at that place.

Why is mercury used as a barometric liquid ? This is on account of the following two reasons :

(*i*) The height of the column in a barometer is inversely proportional to the density of the liquid. As mercury has very high density, the height of the column set up is very convenient for study.

(*ii*) Mercury is non-volatile at room temperature. Hence the vapour pressure due to mercury vapours is negligible.

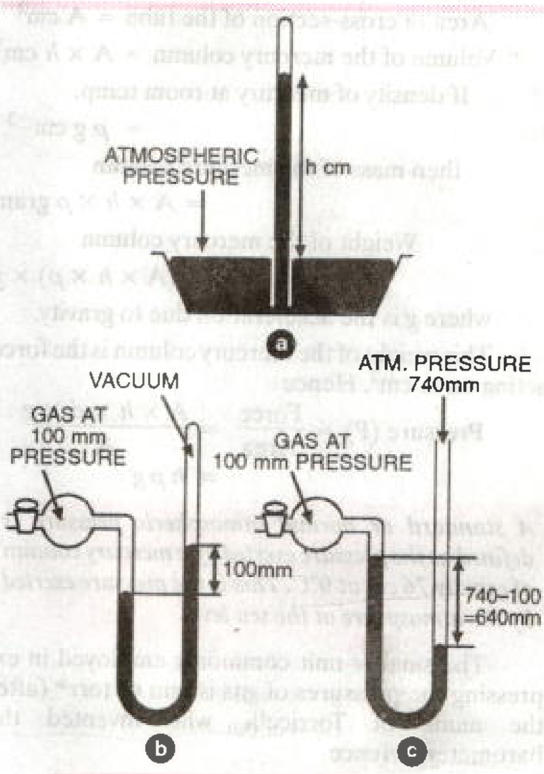

FIGURE 2.1. (a) Barometer (b) Closed limb manometer (c) Open limb manometer.

The instrument used for the measurement of the pressure of a gas is called a **manometer.** It simply consists of a U-shaped tube containing mercury usually. One limb of the tube is longer than the other. Two types of manometers are used. These are :

(*i*) Those in which the longer limb is closed (Fig. 2.1. *b*)

(*ii*) Those in which the longer limb is open (Fig. 2.1. *c*)

Closed limb manometer is used only for gases at pressures less than the atmospheric pressure. The open limb manometer is used for all cases. In case the gas pressure is greater than atmospheric pressure, mercury stands at a higher level in the longer limb. In such a case, the difference of levels is added to the atmospheric pressure to get the pressure of the gas.

As pressure is force per unit area, the pressure obtained in terms of the height of the mercury column can be converted into force per unit area as follows :

Suppose height of the mercury column $= h$ cm

Area of cross-section of the tube $=$ A cm^2

$\therefore$ Volume of the mercury column $= \text{A} \times h$ cm^3

If density of mercury at room temp. $= \rho$ g cm^{-3}

then mass of the mercury column $= \text{A} \times h \times \rho$ gram

$\therefore$ Weight of the mercury column $= (\text{A} \times h \times \rho) \times g$

where g is the acceleration due to gravity.

This weight of the mercury column is the force acting on A cm^2. Hence

$$\text{Pressure (P)} = \frac{\text{Force}}{\text{Area}} = \frac{\text{A} \times h \times \rho \times g}{\text{A}} = h \rho g$$

A standard or normal atmospheric pressure is defined as the pressure exerted by a mercury column of exactly 76 cm at 0°C. This is the pressure exerted by the atmosphere at the sea level.

The smaller unit commonly employed in expressing the pressures of gas is mm or torr* (after the name of Torricelli, who invented the barometer). Hence

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

However, the unit of pressure now commonly used is 'bar'.

$$\boxed{\begin{aligned} 1 \text{ atm} &= 1{\cdot}01325 \text{ bar} \\ \text{or} \quad 1 \text{ bar} &= 0{\cdot}987 \text{ atm} \end{aligned}}$$

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

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

The two units are related as

$$\boxed{\begin{aligned} 1 \text{ atm} &= 101,325 \text{ Pa or Nm}^{-2} \\ &= 1.01325 \times 10^5 \text{ Pa or Nm}^{-2} \\ 1 \text{ bar} &= 10^5 \text{ Pa or Nm}^{-2} \end{aligned}}$$

A bigger unit, called kilopascals (written as kPa) is also sometimes used. Thus

$$1 \text{ bar} = 10^2 \text{ kPa}$$

EXAMPLE. *A manomter is connected to a gas containing bulb. The open arm reads 43·7 cm whereas the arm connected to the bulb reads 15·6 cm. If the barometric pressure is 743 mm mercury, what is the pressure of gas in bar ?* **(N.C.E.R.T.)**

Solution. Difference of mercury levels in the two arms $= 43{\cdot}7 - 15{\cdot}6 \text{ cm} = 28{\cdot}1 \text{ cm}$

As level in the limb connected to the bulb is lower than that of the open limb, this means pressure of gas is more than the atmospheric pressure.

$\therefore$ Pressure of the gas in the bulb

$=$ Barometric pressure

$+$ Difference of mercury levels

$$= 74{\cdot}3 \text{ cm} + 28{\cdot}1 \text{ cm} = 102{\cdot}4 \text{ cm}$$

$$= \frac{102{\cdot}4}{76} \text{ atm} = \frac{102{\cdot}4}{76} \times 1{\cdot}01325 \text{ bar}$$

$$= \mathbf{1{\cdot}365 \text{ bar}}$$

(4) Measurement of Temperature. Temperature is a measure of the extent of hotness or coldness of a body. The measurement of temperature is based upon the principle that substances expand on heating. The most common substance whose expansion is made use of in the measurement of temperatures is 'mercury'. There are three different scales on which the temperatures are measured. These are

(*i*) Centigrade or Celsius scale (after the name of Anders Celsius)

(*ii*) Fahrenheit scale (after the name of Daniel Fahrenheit, a German instrument maker)

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* The International Committee of Weights and Measures recommends that the use of 'torr' should be dropped.

(*iii*) Kelvin scale (after the name of Lord Kelvin)

The Celsius scale is based upon taking the freezing point of water as 0°C and the boiling point of water as 100°C at normal atmospheric pressure (*i.e.* at sea level) and then dividing the range into 100 equal parts so that each part represents 1°C.

The Fahrenheit scale is based upon taking the freezing point of water as 32 °F and the boiling point of water as 212 °F and dividing the range into 180 equal parts. Thus

100 Celsius degrees = 180 Fahrenheit degrees

or 5 Celsius degrees = 9 Fahrenheit degrees*

The Kelvin scale of temperatures has emerged as a result of study on gases. It is possible to cool a substance below 0°C and thus we can have negative temperatures. But experimentally it is found that it is not possible to cool a gas below − 273.15°C as after that the gas ceases to exist. Thus this is the lowest temperature that can be attained and hence is taken as 0 K on the Kelvin scale. Negative Kelvin temperatures are as impossible as negative volumes or negative lengths. Thus

$$-273.15^\circ C = 0\ K$$

or $$0^\circ C = 273.15\ K$$

The size of Kelvin degree is same as that of Celsius degree so that

$$\boxed{t^\circ C = t + 273.15\ K}$$

Kelvin is the SI unit of temperature and according to SI, it should be written without putting the symbol of degree (°) *e.g.* 100°K should be written as 100K.

2.4. Gas Laws

(1) BOYLE'S LAW

The first quantitative relationship between the volume and pressure of a gas was studied experimentally by Robert Boyle in 1662. The studies were made with air at room temperature. He used mercury and a simple U-tube of the type shown in Fig. 2.2. The pressure was increased by putting more mercury into the open limb. The volume of the air enclosed in the space above mercury in the shorter limb was noted each time. Similar experiments were repeated with other gases.

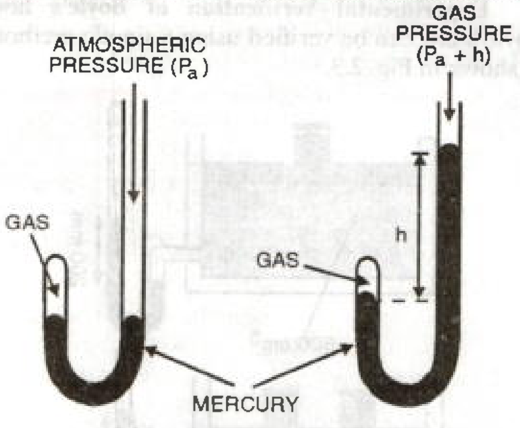

FIGURE 2.2. Boyle's apparatus for study of effect of pressure on the volume of air at room temperature

The following generalization was observed which is known as Boyle's law :

Temperature remaining constant, the volume of a given mass of a gas is inversely proportional to its pressure.

Mathematically, Boyle's law may be stated as

$V \propto \frac{1}{P}$ for a given mass of a gas at constant temperature

or $$V = k.\frac{1}{P} \quad \text{or} \quad PV = k$$

i.e. $$\boxed{PV = \text{constant at constant temperature}}$$

where P and V represent the pressure and volume of the gas and *k* is a constant whose value depends upon the mass of the gas and temperature.

Thus Boyle's law may also be stated as follows:

Temperature remaining constant, the product of pressure and volume of a given mass of a gas is constant.

Thus if P_1 and V_1 are the initial pressure and volume of a gas and keeping the temperature constant, if pressure is changed to P_2, then volume will change to V_2 (say) such that according to Boyle's law

$$\boxed{P_1 V_1 = P_2 V_2 \text{ at constant temperature}}$$

This form of Boyle's law is very helpful in solving numerical problems because knowing any three variables, the fourth can be calculated.

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* The conversion method will be $^\circ C = \frac{5}{9}(^\circ F - 32)$ or $^\circ F = \frac{9}{5}(^\circ C) + 32$.

Experimental Verification of Boyle's law. Boyle's law can be verified using a simple method as shown in Fig. 2.3.

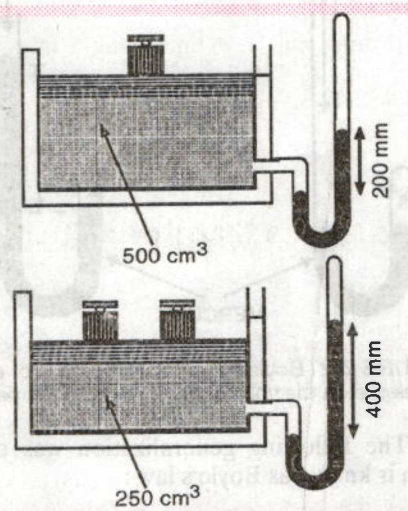


FIGURE 2.3. Verification of Boyle's law.

We observe that if the pressure is doubled at constant temperature, the volume is reduced to half. Similarly if pressure is made four times, the volume is reduced to 1/4 th and so on.

Graphical Verification of Boyle's law. According to Boyle's law

$$P \propto \frac{1}{V} \quad \text{or} \quad PV = \text{constant}$$

Thus the law can be verified by plotting

(*i*) P *vs* $\frac{1}{V}$ when a straight line passing through the origin is obtained (Fig. 2.4 *a*), or

(*ii*) PV *vs* P when a straight line parallel to the X-axis is obtained (Fig. 2.4*b*), or

(*iii*) V *vs* P when branch of hyperbola in the first quadrant is obtained (Fig. 2.4 *c*).

It is interesting to note that in the equation PV = constant, the value of the constant depends upon the amount of the gas taken (*i.e.* no. of moles *n*) and the temperature (T). Hence for a given amount of the gas taken, a different P – V curve is obtained at each temperature. Such a P – V curve at constant temperature is called an **isotherm.** Three such isotherms are shown in Fig. 2.5 below :

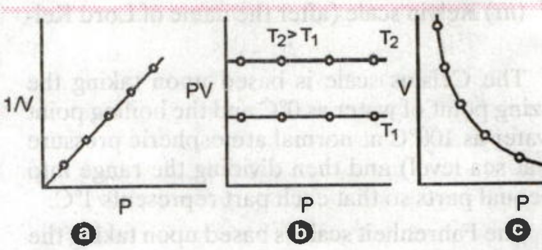


FIGURE 2.4. Graphical verification of Boyle's law.

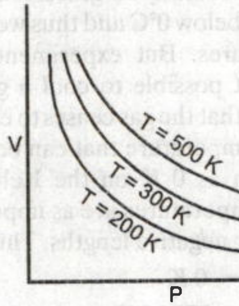


FIGURE 2.5. Isotherms for a definite amount of the gas.

Significance of Boyle's Law. Boyle's law proves a very important fact that the gases are compressible. The more it is pressed, the denser it becomes. Hence it can be concluded that *at constant temperature, the gas density is directly proportional to pressure.*

At altitudes, as the atmospheric pressure is low, the air is less dense. As a result, less oxygen is available for breathing. The person feels uneasiness, headache etc. This is called **altitude sickness.** That is why the mountaineers have to carry oxygen cylinders with them.

PROBLEMS ON BOYLE'S LAW

EXAMPLE 1. *A vessel of 120 ml capacity contains a certain mass of a gas at 20°C and 750 mm pressure. The gas was transferred to a vessel whose volume is 180 ml. Calculate the pressure of the gas at 20°C.*

Solution. Since a gas completely fills the vessel in which it is contained, therefore we have :

$$V_1 = 120 \text{ ml}, \; V_2 = 180 \text{ ml}$$

$$P_1 = 750 \text{ mm} \quad P_2 = ? \text{ mm}$$

Since the temperature remains constant, therefore, by applying Boyle's Law,

$$P_1 V_1 = P_2 V_2$$

Substituting the corresponding values, we have

$$750 \times 120 = P_2 \times 180$$

or $$P_2 = \frac{750 \times 120}{180} = 500 \text{ mm}$$

∴ Pressure of the gas = **500 mm**

EXAMPLE 2. *103 ml of carbon dioxide were collected at 27°C and 763 mm pressure. What will be its volume if the pressure is changed to 721 mm at the same temperature ?*

Solution.

Given Conditions	*Final Conditions*
$V_1 = 103$ ml	$V_2 = ?$ ml
$P_1 = 763$ mm	$P_2 = 721$ mm

By applying Boyle's Law since temperature is constant,

$$P_2 \times V_2 = P_1 \times V_1.$$

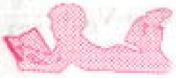
Substituting the corresponding values, we have

$$721 \times V_2 = 763 \times 103$$

$$V_2 = \frac{763 \times 103}{721} = 109 \text{ ml}$$

∴ Volume of carbon dioxide = **109 ml.**

PROBLEMS FOR PRACTICE



1. A certain mass of a gas occupies 39 ml at 760 mm pressure. What volume would it occupy if the pressure is raised to 780 mm provided that temperature remains constant ? **[Ans. 38.0 ml]**
2. 200 ml of a gas are found to have a pressure of 750 mm. What will be its volume if the pressure is doubled at the same temperature ? **[Ans. 100.0 ml]**
3. A vessel is 120 mL capacity contains a certain amount of gas at 35°C and 1·2 bar pressure. The gas is transferred to another vessel of volume 180 mL at 35°C. What would be its pressure ? *(N.C.E.R.T.)* **[Ans. 0·8 bar]**
4. A balloon filled with an ideal gas is taken from the surface of the sea deep to a depth of 100 m. What will be its volume in terms of its original volume ? **[Ans. 9·3% of its volume at the surface]**
5. A bulb 'X' of unknown volume containing a gas at one atmospheric pressure is connected to an evacuated bulb of 0·5 litre capacity through a stop-cock. On opening the stop-cock, the pressure in the whole system after some time was found to have a constant value of 570 mm at the same temperature. What is the volume of the bulb X? **[Ans. 1·5 litre]**
6. What will be the minimum pressure required to compress 500 dm³ of air at 1 bar to 200 dm³ at 30° ? *(N.C.E.R.T.)* **[Ans. 2·5 bar]**
7. A gas occupies a volume of 2·5 L at 9×10^5 Nm^{-2}. Calculate the additional pressure required to decrease the volume of the gas to 1·5 L, keeping the temperature constant. **[Ans. 6×10^5 Nm^{-2}]**

HINTS FOR DIFFICULT PROBLEMS

3. $P_1V_1 = P_2V_2$ *i.e.* $1{\cdot}2 \times 120 = P_2 \times 180$

   or $P_2 = 0{\cdot}8$ bar

4. Pressure at the surface = 76 cm of Hg

   $= 76 \times 13{\cdot}6$ cm of $H_2O = 10{\cdot}3$ *m* of H_2O

   ∴ Pressure at 100 *m* depth

   $= 100 + 10{\cdot}3\,m = 110{\cdot}3\,m$

   Applying $P_1V_1 = P_2V_2$,

   (At surface) (At 100 *m* depth)

   $10{\cdot}3 \times V = 110{\cdot}3 \times V_2$

   or $V_2 = 0{\cdot}093\,V = 9{\cdot}3\%$ of V

5. Suppose volume of the bulb X = V

   i.e. $V_1 = V$ and $P_1 = 1$ atm

   After connecting to bulb of 0·5 L capacity, volume = (V + 0·5 L)

   i.e. $V_2 = (V + 0{\cdot}5)$ L, $P_2 = 570$ mm $= 570 / 760$ atm

   Apply $P_1V_1 = P_2V_2$, calculate V.

7. $V_1 = 2{\cdot}5$ L, $P_1 = 9 \times 10^5$ Nm^{-2} ;

   $V_2 = 1{\cdot}5$ L, $P_2 = ?$

   Apply $P_1V_1 = P_2V_2$. Calculate P_2. We get $P_2 = 15 \times 10^6$ Nm^{-2}. Additional pressure required

   $= 15 \times 10^6$ Nm^{-2} $- 9 \times 10^5$ Nm^{-2}

   $= 6 \times 10^5$ Nm^{-2}.

(2) CHARLES' LAW

Studies on the effect of temperature on the volume of a gas at constant pressure were first carried out by the French scientist, Jacques Charles in 1787 and then extended by Joseph Gay Lussac in 1802. The following generalization was observed which is known as Charles' law :

Pressure remaining constant, the volume of a given mass of a gas increases or decreases by 1/273 of its volume at 0°C for every one degree centigrade rise or fall in temperature.

Mathematically,

$$\boxed{\begin{aligned} V_t &= V_0 + \frac{V_0}{273} \times t \\ &= V_0\left(1 + \frac{t}{273}\right) = V_0\left(\frac{273 + t}{273}\right) \end{aligned}}$$

where V_t is the volume of the gas at t°C and V_0 is its volume at 0°C.

The volume of a certain mass of a gas at any temperature can be calculated by the application of the above relation. Thus :

$$\text{Volume at } 10°\text{C} = V_0 + \frac{V_0 \times 10}{273}$$

$$\text{Volume at } 1°\text{C} = V_0 + \frac{V_0}{273}$$

$$\text{Volume at } -1°\text{C} = V_0 - \frac{V_0}{273}$$

$$\text{Volume at } -20°\text{C} = V_0 - \frac{20\ V_0}{273}$$

$$\text{Volume at } -273°\text{C} = V_0 - \frac{273\ V_0}{273} = 0$$

This implies that a gas at −273°C will have zero or no volume, *i.e.*, it will cease to exist. Below this temperature in volume will be negative which is meaningless. In fact, no one has ever traced the rate of contraction in volume of any gas upto −273°C at constant pressure. In actual practice, all gases liquefy before this temperature is reached.

The same conclusion can also be reached graphically by plotting the volume of a certain mass of a gas (along y-axis) against temperature (along x-axis) at constant pressure. We get a graph consisting of a straight line as shown in Fig. 2.6.

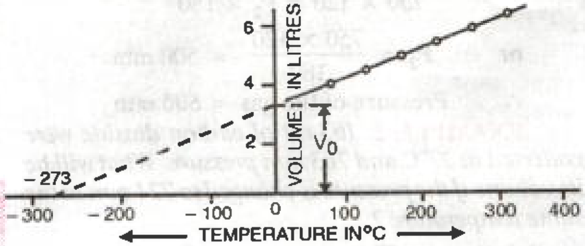


FIGURE 2.6. Volume of a gas as function of temperature in centigrade.

If we extrapolate this straight line, it will meet the temperature axis at −273°C. Thus, at −273°C, a gas occupies zero or no volume. This temperature has never been realized in any laboratory of the world so far.

It is interesting to note that the straight line V−t plots obtained for different amounts of the same gas or for same amount of the different gases are different but each of them intersects the temperature axis at −273°C corresponding to zero volume as shown in Fig. 2.7 below :

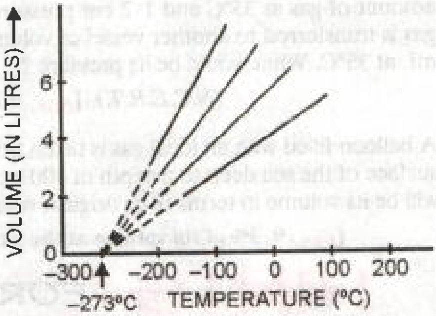


FIGURE 2.7. Plots of volume (in L) versus temperature (in °C) for different amounts of a gas at constant pressure (atmospheric pressure)

Absolute Zero and Absolute Scale of Temperature.

The lowest possible hypothetical or theoretical temperature of —273°C at which a gas is supposed to have zero volume is called Absolute zero.

More careful experiments have shown that the absolute zero of temperature is −273.15°C. However, for most of the purposes, the approximate value of −273°C is used.

Lord Kelvin has suggested a new scale of temperature starting with −273°C as its zero. This scale of temperature is known as Kelvin scale or

Absolute Scale. The size of the degree on the Kelvin scale is the same as that on the centigrade scale. On this scale, the freezing point of water, *i.e.*, 0°C is 273° A. (Absolute) or 273 K (Kelvin). Thus, any temperature on the centigrade scale can be converted to that on the Kelvin scale by just adding 273 to its value on the centigrade scale. Hence, the two scales are connected by the relation :

Kelvin Temperature = Centigrade temperature + 273

$$\text{or} \qquad \boxed{\text{TK} = t^\circ\text{C} + 273}$$

where T and t° are the temperatures on the Kelvin and the Centigrade scales respectively. This scale of temperature is also called *Thermodynamic scale of temperature*.

A comparison of Celsius, Kelvin and Fahrenheit scales of temperature is given in Fig. 2.8 below :

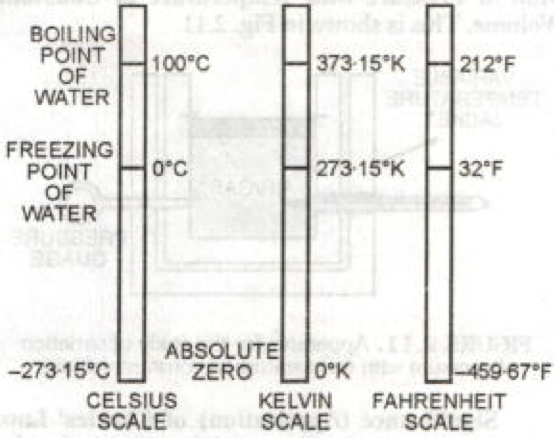


FIGURE 2.8. Comparison of Celsius, Kelvin and Fahrenheit scales of temperature.

The advantage of kelvin scale lies in the fact that the volume of a gas and its temperature on the Kelvin scale are directly proportional to each other. This can be explained as follows :

According to Charles' law in the form already defined

$$V_t = V_0 \left(\frac{273 + t}{273}\right)$$

Putting $273 + t = \text{T}$, the corresponding temperature on the Kelvin scale, we get

$$V_t = V_0 \frac{\text{T}}{273}$$

As V_0 and 273 are constant, hence

$$V_t \propto \text{T} \quad \text{or simply,} \quad V \propto \text{T}$$

$$\text{or} \qquad V = k\text{T}$$

The numerical value of the constant k depends upon the amount of the gas taken and the pressure.

The above relation gives another definition of Charles' law as follows :

Pressure remaining constant, the volume of a given mass of a gas is directly proportional to its temperature in degrees Kelvin.

The relation V ∝ T implies that

$$\boxed{\frac{V}{T} = \text{Constant at constant pressure.}}$$

Thus if V_1 is the volume of the gas at temperature T_1 (in degrees Kelvin) and keeping the pressure constant, temperature is changed to T_2, then the volume will change to V_2 such that

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ at constant pressure}}$$

This form of Charles' law is very helpful in solving numerical problems because knowing any three variables the fourth can be calculated.

Thus a plot of V *vs* T at constant pressure will be a straight line passing through the origin (Fig. 2.9).

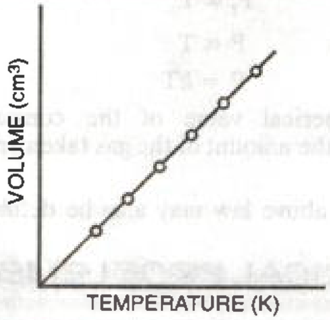


FIGURE 2.9. Plot of V vs T at constant P.

Experimental Set-up for the Study of Variation of Volume with Temperature at Constant Pressure. This is shown in Fig. 2.10.

Variation of Pressure with Temperature at Constant Volume (Amonton's law). The law which governs the relationship between pressure and temperature of a gas at constant volume is similar to that between volume and temperature at constant pressure. It states as under :

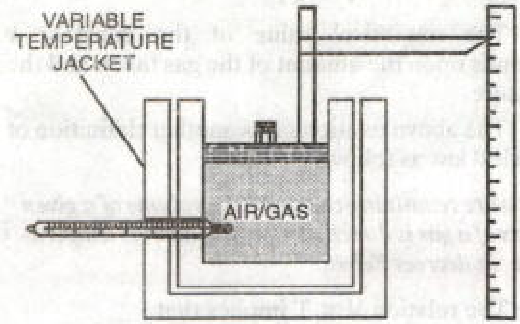


FIGURE 2.10. Apparatus for the study of variation of volume with temperature at constant pressure.

Volume remaining constant, the pressure of a given mass of a gas increases or decreases by 1/273 of its pressure at 0°C for every 1°C rise or fall in temperature.

Mathematically,

$$P_t = P_0\left(1+\frac{t}{273}\right) = P_0\left(\frac{273+t}{273}\right) = P_0\,\frac{T}{273}$$

where P_t and P_0 are the pressures of a certain amount of a gas at t°C and 0°C respectively.

As P_0 and 273 are constants, hence

$$P_t \propto T$$

or simply $\quad P \propto T$

i.e. $\quad P = kT$

The numerical value of the constant k depends upon the amount of the gas taken and the volume.

Thus the above law may also be defined as follows :

Volume remaining constant, the pressure of a given mass of a gas is directly proportional to its temperature in degrees Kelvin.

The generalisation, as given above, is referred to as **Pressure – Temperature Law** or **Amonton's law.**

In 1703, G. Amonton constructed an air thermometer based on the principle that the pressure of a gas is a measure of the temperature of the gas.

The relation $P \propto T$ implies that

$$\frac{P}{T} = \text{Constant at constant volume}$$

which means that

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

Experimental Set up for the Study of Variation of Pressure with Temperature at Constant Volume. This is shown in Fig. 2.11.

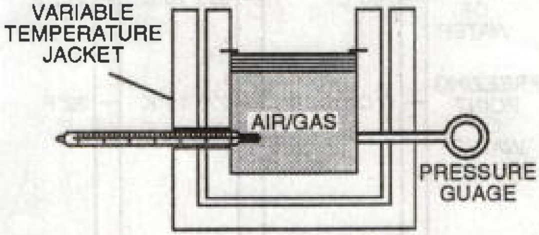


FIGURE 2.11. Apparatus for the study of variation of pressure with temperature at constant volume.

Significance (Application) of Charles' Law. Air expands on heating and hence its density decreases. Thus hot air is lighter than the atmospheric air. This fact is made use of in filling hot air in the balloons which rise up for meteorological observations.

NUMERICAL PROBLEMS ON CHARLES' LAW AND AMONTON'S LAW

EXAMPLE 1. *20 ml of hydrogen measured at 15°C are heated to 35°C. What is the new volume at the same pressure ?*

Solution.

Given conditions	*Final conditions*
$V_1 = 20$ ml	$V_2 = ?$ ml
$T_1 = 15 + 273 = 288$ K	$T_2 = 35 + 273 = 308$K

By applying Charles' Law

$$\frac{V_2}{308} = \frac{20}{288}$$

$$V_2 = \frac{20}{288} \times 308 = 21{\cdot}38$$

Volume of hydrogen gas at 35°C

$$= 21{\cdot}38 \text{ ml.}$$

EXAMPLE 2. *At what temperature centigrade will the volume of a gas at 0°C double itself, pressure remaining constant ?*

Solution.

Let the volume of the gas at 0°C = V ml

Thus, we have :

$V_1 = V$ ml, $\quad V_2 = 2V$ ml

$T_1 = 0 + 273 = 273$ K $\quad T_2 = ?$

By applying, Charles' Law, $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

Substituting the corresponding values, we have

$$\frac{V}{273} = \frac{2V}{T_2}$$

$$T_2 = \frac{2V \times 273}{V} = 546 \text{ K}$$

$$\therefore \quad T_2 = 546 - 273 = \mathbf{273°C}$$

EXAMPLE 3. *A 10·0 litre container is filled with a gas to a pressure of 2·00 atm at 0°C. At what temperature will the pressure inside the container be 2·50 atm ?*

Solution. As volume of the container remains constant, applying pressure – temperature law viz.

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}, \text{ we get } \frac{2 \text{ atm}}{273 \text{ K}} = \frac{2·50 \text{ atm}}{T_2}$$

or $\quad T_2 = 341$ K $= 341 - 273$°C $=$ **68°C**

EXAMPLE 4. *A student set up the apparatus at room temperature (27°C). By mistake without adding the reaction mixture he started heating the flask. By the time he realised his mistake, the temperature had shot up to 477°C as recorded by a pyrometer. What fraction of air would have been expelled out ?* **(N.C.E.R.T.)**

Solution. Suppose volume of vessel = V cm^3 *i.e.* volume of air in the flask at 27°C = V cm^3.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad i.e. \quad \frac{V}{300} = \frac{V_2}{750}$$

or $\quad V_2 = 2·5$ V

$\therefore$ Volume expelled $= 2·5\text{ V} - \text{V} = 1·5$ V

$\therefore$ Fraction of air expelled $= \dfrac{1·5\text{ V}}{2·5\text{ V}} = \dfrac{3}{5}$

EXAMPLE 5. *An open vessel contains 200 mg of air at 17°C. What weight percent of air would be expelled if the vessel is heated to 117°C ?*

Solution. Suppose volume of 200 mg of air at 17°C = V ml

As pressure remains constant (being an open vessel)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \text{ gives } \frac{V}{290} = \frac{V_2}{390} \text{ or } V_2 \ 1·34 \text{ V}$$

$\therefore$ Volume of air expelled $= 1·34\text{ V} - \text{V} = 0·34$ V

Mass of 1·34 V air at 117°C = 200 mg

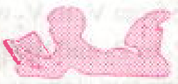
Mass of 0·34 V air at 117°C

$$= \frac{200}{1·34} \times 0·34 \text{ mg}$$

$\therefore$ Mass % of air expelled

$$= \frac{200 \times 0·34}{1·34} \times \frac{1}{200} \times 100 = 25·37\%$$

PROBLEMS FOR PRACTICE



1. 300 ml of oxygen gas at —10°C are heated to 10°C. What is the new volume if pressure remains constant ? **[Ans. 322.8 ml]**
2. 25 dm^3 of ammonia at 283 K are heated until its volume is 30 dm^3. To what temperature must it have been raised to accomplish the change ? **[Ans. 339.6 K]**
3. What will be the volume of hydrogen when 3 litres of it are cooled from 15°C to —73°C at constant pressure ? **[Ans. 2.0833 litres]**
4. What volume of air will be expelled from a vessel containing 400 cm^3 at 7°C when it is heated to 27°C at the same pressure ? **[Ans. 28.6 cm^3]**
5. A steel tank containing air at 15 atm pressure at 15°C is provided with a safety valve that will yield at a pressure of 30 atm. To what minimum temperature must the air be heated to blow the safety valve ? **[Ans. 303°C]**
6. It is desired to increase of the volume of a gas by 20% without changing the pressure. To what temperature, the gas must be heated if the initial temperature of the gas is 27° ? **[Ans. 87°C]**
7. A gas cylinder containing cooking gas can withstand a pressure of 14·9 atmospheres. The pressure gauge of the cylinder indicates 12 atmosphere at 27°C. Due to sudden fire in the building, the temperature starts rising. At what temperature the cylinder will explode ? **[Ans. 99·5°C]**

HINTS FOR DIFFICULT PROBLEMS

4. $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$ *i.e.* $\dfrac{400 \text{ cm}^3}{(273+7)\text{ K}} = \dfrac{V_2}{(273+27)\text{ K}}$

or $\quad V_2 = \dfrac{400}{280} \times 300 \text{ cm}^3 = 482·6 \text{ cm}^3.$

This is the volume after expansion.

$\therefore$ Volume expelled

$= (428·6 - 400))$ cm^3 $= 28·6$ cm^3.

HINTS CONTD.

5. $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ *i.e.* $\frac{15 \text{ atm}}{288 \text{ K}} = \frac{30 \text{ atm}}{T_2}$ or $T_2 = 576$ K

$= (576—273)°\text{C} = 303°\text{C}$

6. Suppose volume of gas at 27°C = V cm^3

Increase in volume desired = 20% of V

$= \frac{20}{100} \times V = 0{\cdot}2\ V$

∴ Final volume = V + 0·2 V = 1·2 V

Now $V_1 = V\ \text{cm}^3$, $T_1 = 300$ K, $V_2 = 1{\cdot}2$ V,

$T_2 = ?$ At constant P, $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ ∴ $\frac{V}{300} = \frac{1{\cdot}2\ V}{T_2}$

or $T_2 = 360$ K $= 360 - 273°\text{C} = 87°\text{C}$.

7. $P_1 = 12$ atm, $T_1 = 300$ K, $P_2 = 14{\cdot}9$ atm, $T_2 = ?$

As volume of the cylinder is constant, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$.

(3) IDEAL GAS EQUATION/EQUATION OF STATE FOR AN IDEAL GAS

Boyle's law gives the effect of pressure on the volume of a gas at constant temperature whereas Charles' law gives the effect of temperature on the volume of a gas at constant pressure. However, it is possible to derive an equation which gives the simultaneous effect of pressure and temperature on the volume of a gas.

The equation which gives the simultaneous effect of pressure and temperature on the volume of a gas is known as ideal gas equation or equation of state for an ideal gas.

Derivation. The gas equation may be derived from Boyle's and Charles' law as explained below :

Let the volume of a certain mass of a gas change from V_1 to V_2 when the pressure is changed from P_1 to P_2 and temperature from T_1 to T_2 in the following two steps as shown in Fig. 2.12.

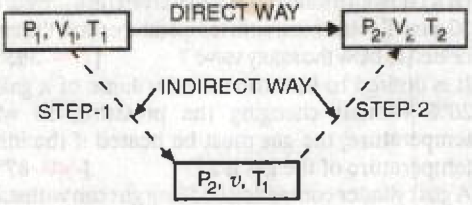


FIGURE 2.12. Change of state assumed to be taking place in two steps.

Step 1. First suppose that the volume of a given mass of a gas changes from V_1 to v when the pressure is changed from P_1 to P_2 at constant temperature T_1.

Then according to Boyle's Law,

$$P_2 \times v = P_1 \times V_1$$

$$\text{or} \quad v = \frac{P_1 V_1}{P_2} \quad \text{...}(i)$$

Step 2. Now suppose that the volume v changes to V_2 when the temperature is changed from T_1 to T_2 at constant pressure P_2.

$$\therefore \quad \frac{v}{T_1} = \frac{V_2}{T_2}$$

$$\text{or} \quad V_2 = v \times \frac{T_2}{T_1} \quad \text{...}(ii)$$

Substituting the value of v from Eq. (*i*) in Eq. (*ii*), we have

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

$$\boxed{\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}} \quad \text{...}(iii)$$

This is the most convenient form of the ideal gas equation for the purpose of calculations when any five variables are given and 6th is to be calculated.

Another popular form of the ideal gas equation can be obtained as follows :

Eqn. (*iii*) implies that $\frac{P \times V}{T}$ = Constant

= K (say)

The value of the constant K depends only upon the amount of the gas taken. If n is the number of moles of the gas taken, then it is found that

$$K \propto n$$

$$\text{or} \quad K = nR \quad \text{...}(iv)$$

where R is a constant of proportionality and is found to be independent of the nature of the gas and depends only on the amount of the gas taken. For 1 mole of any gas, the value of R is the same. Hence R is called *'universal gas constant'*.

Substituting the value of K in eqn (*iii*), we get

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

$$\text{or} \qquad \boxed{PV = nRT} \qquad ...(v)$$

This is the most common form of the ideal gas equation.

Alternative Derivation of Ideal Gas Equation. The ideal gas equation can be derived directly by combining Boyle's law, Charles' law and Avogadro's law as follows :

According to Boyle's law,

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

According to Charles' law,

$$V \propto T \text{ at constant P} \qquad ...(vii)$$

According to Avogadro's law,

$$V \propto n \text{ at constant T and P} \qquad ...(viii)$$

where n is the number of moles of the gas. (This is because according to Avogadro's law, equal volumes of different gases contain equal number of molecules under similar conditions of temperature and pressures. In other words, volume is directly proportional to the number of molecules which in turn is directly proportional to the number of moles of the gas.)

Combining (*vi*), (*vii*) and (*viii*), we get

$$V \propto \frac{1}{P} \times T \times n$$

$$V = R \times \frac{1}{P} \times T \times n$$

$$\text{or} \qquad PV = nRT$$

where, as before, R is molar gas constant.

For 1 mole of the gas, the ideal gas equation becomes

$$PV = RT$$

A gas that obeys ideal gas equation exactly is called an *ideal gas*.

An ideal gas equation is also called the equation of state because it defines the state of the gas completely when all the variables have been specified.

Ideal gas equation in terms of density. This form of the ideal gas equation may be derived as follows :

If m is the mass of the gas in grams and M is the molecular mass of the gas, then

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

$$\therefore \qquad PV = n\,RT = \frac{m}{M}\,RT$$

$$\text{or} \qquad P = \frac{m}{V}\,\frac{RT}{M} = d\,\frac{RT}{M}$$

$$\text{or} \qquad \boxed{M = d\,\frac{RT}{P}} \qquad ...(viii)$$

This expression can be used for the calculation of molecular mass from a known value of density of the gas at a given temperature and pressure. Alternatively, the expression (*viii*) can be used for the calculation of any one quantity from known values of the other quantities involved.

Deduction of Avogadro's Law from Ideal gas law. According to ideal gas law

$$PV = nRT$$

Thus if two gases have the same values of P and T, then if their volumes V are equal, the values of n must be same. In other words, same volumes of different gases under same conditions of pressure and temperature must contain the same number of moles which in turn will contain the same number of molecules (because 1 mole of any gas contains the same number of molecules viz. 6.022×10^{23})

Standard or Normal Temperature and Pressure (STP or NTP). It is obvious from the above discussion that the volume of a given mass of a gas changes when temperature and pressure are changed. Thus, to compare the results of experiments involving volumes of different gases, it is necessary to reduce the volume to certain standard conditions of temperature and pressure. The standard temperature is 0°C or 273 K while the standard pressure is one atmosphere at sea level or 760 mm or 76 cm of mercury. These standard conditions are known as Standard Temperature and Pressure *i.e.* STP or Normal Temperature and Pressure *i.e.* NTP. *The standard pressure now commonly used is 1 bar instead of 1 atm.* Thus

STP or NTP implies that

Temperature $= 0°C = 273{\cdot}15\,K \simeq 273\,K$

Pressure $= 1\,atm = 76\,cm = 760\,mm = 760\,torr$
$= 101.325\,k\,Pa$

or Pressure $= 1\,bar = 10^5\,Pa = 10^2\,kPa$

IMPORTANT

At STP i.e. 0°C and 1 atm pressure, 1 mole of any gas has a volume equal to 22400 cm³. But at 1 bar pressure and 0°C, the volume occupied by 1 mole of the gas is 22700 cm³ i.e. 22·7 dm³ or $22{\cdot}7 \times 10^{-3}\,m^3$.

Nature and Values of the Gas Constant R. From the gas equation, PV = n RT, we have

$$R = \frac{P \times V}{n \times T} = \frac{\text{Pressure} \times \text{Volume}}{\text{Moles} \times \text{Temp. in °K}}$$

$$= \frac{\frac{\text{Force}}{\text{Area}} \times (\text{Length})^3}{\text{Moles} \times \text{Degrees}} = \frac{\frac{\text{Force}}{(\text{Length})^2} \times (\text{Length})^3}{\text{Moles} \times \text{Degrees}}$$

$$= \frac{\text{Force} \times \text{Length}}{\text{Moles} \times \text{Degrees}} = \frac{\text{Work}}{\text{Moles} \times \text{Degrees}}$$

= **Work done per degree per mole**

Thus R may be expressed in different units depending upon the units of work.

Numerical Value of the Gas Constant (R).

(*i*) *At N.T.P. conditions, for 1 mole of the gas*

P = 1 atmosphere, V = 22·4 litres,
T = 273 K, n = 1 mole

$$\therefore \; R = \frac{P \times V}{n \times T} = \frac{1 \text{ atm} \times 22\cdot4 \text{ L}}{1 \text{ mol} \times 273 \text{ K}}$$

$$= \mathbf{0\cdot0821 \text{ litre atmosphere degree}^{-1} \text{ mol}^{-1}}$$

If V = 22400 cm^3,

$$R = \mathbf{82\cdot1 \text{ cm}^3 \text{ atm deg}^{-1} \text{ mol}^{-1}}$$

or Taking P = 1 bar so that

$$V = 22\cdot7 \text{ dm}^3,$$

$$R = \frac{1 \text{ bar} \times 22\cdot7 \text{ dm}^3}{1 \text{ mol} \times 273 \text{ K}}$$

$$= \mathbf{0\cdot083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}}$$

(*ii*) *In the C.G.S. units, for 1 mole of the gas at N.T.P.*

P = 76 cm = 76 × 13·6 × 981 dynes/sq. cm
V = 22400 ml, T = 273 K, n = 1 mole

$$\therefore R = \frac{P \times V}{n \times T} = \frac{(76 \times 13\cdot6 \times 981) \times 22400}{1 \times 273}$$

$$= \mathbf{8\cdot314 \times 10^7 \text{ ergs degree}^{-1} \text{ mol}^{-1}}$$

(*iii*) *For expressing R in SI units,* put

$$10^7 \text{ ergs} = 1 \text{ joule.}$$

$$\text{Hence } R = \frac{8\cdot314 \times 10^7}{10^7} \text{ joules degree}^{-1} \text{ mol}^{-1}$$

$$= 8\cdot314 \text{ joules degree}^{-1} \text{ mol}^{-1}$$

$$= \mathbf{8\cdot314 \text{ JK}^{-1} \text{ mol}^{-1}}$$

or directly taking P = 101325 Nm^{-2} or Pa,

V = 0·0224 m^3, T = 273 K

we get R = 8·314 J K^{-1} mol^{-1}

or taking P = 101·325 kPa,

V = 22·4 dm^3,

T = 273 K

we get **R = 8·314 kPa dm^3 K^{-1} mol^{-1}**

(*iv*) *To express in terms of calories,* we know that 4·184 joules = 1 calorie

$$\text{Hence } R = \frac{8\cdot314}{4\cdot184} \text{ calories degree}^{-1} \text{ mol}^{-1}$$

$$= \mathbf{1\cdot987 \text{ calories degree}^{-1} \text{ mol}^{-1}}$$

To sum up

Units of P	Units of V	Value of R
atmosphere	litres or dm^3	0·0821 L atm K^{-1} mol^{-1} or 0·0821dm^{3}atmK^{-1}mol^{-1}
atmosphere	cm^3	82·1 cm^3 atm K^{-1} mol^{-1}
dynes cm^{-2}	cm^3	8·31×10^7 ergs K^{-1} mol^{-1} =1·987 cal K^{-1} mol^{-1}
N m^{-2} or Pa	m^3	8·314 J K^{-1} mol^{-1}
kPa	dm^3	8·314 kPa dm^3 K^{-1} mol^{-1}
bar	dm^3	**0·083 bar dm^3 K^{-1} mol^{-1}**

NUMERICAL PROBLEMS ON IDEAL GAS EQUATION

TYPE I. Based on the equation $P_1V_1 / T_1 = P_2V_2 / T_2$

EXAMPLE 1. *35 ml of oxygen were collected at 6°C and 758 mm pressure. Calculate its volume at NTP.*

Solution.

Given conditions	*Final conditions*
V_1 = 35 ml	V_2 = ? ml
P_1 = 758 mm	P_2 = 760 mm
T_1=6+273=279 K	T_2=0+273=273K

By applying gas equation, we have

$$\frac{760 \times V_2}{273} = \frac{758 \times 35}{279}$$

$$\therefore \; V_2 = \frac{758 \times 35}{279} \times \frac{273}{760} = 34\cdot16 \text{ ml}$$

Volume of chlorine gas = **34·16 ml.**

EXAMPLE 2. *At 27°C and one atmospheric pressure, a gas has volume V. What will be its volume at 177°C and a pressure of 1.5 atmosphere ?*

Solution.

Given conditions	*Final conditions*
$V_1 = V$	$V_2 = ?$
$P_1 = 1$ atm	$P_2 = 1.5$ atm
$T_1 = 273+27=300$ K	$T_2 = 273+177$ $= 450$K

Applying gas equation, we have

$$\frac{1 \times V}{300} = \frac{1{\cdot}5 \times V_2}{450}$$

$$\therefore \quad V_2 = \frac{1 \times V \times 450}{300 \times 1{\cdot}5} = V$$

$\therefore$ Volume of the gas = V.

EXAMPLE 3. *A sealed tube which can withstand a pressure of 3 atmosphere is filled with air at 27°C and 760 mm pressure. Find the temperature above which it will burst.*

Solution.

Let the volume of air in the tube be V ml.

Given conditions	*New conditions*
V_1 = V ml	V_2 = V ml
P_1 = 760 mm = 1 atm.	P_2 = 3 atm.
$T_1 = 273+27 = 300$K	$T_2 = ?$

By applying gas equation, we have

$$\frac{V \times 1}{300} = \frac{V \times 3}{T_2}$$

$$\therefore \quad T_2 = 300 \times 3 = 900 \text{ K}$$

$P_1 = 760$ m $P_2 = 3$ atm

$V_1 = V$ $V_2 = V$

$T_1 = 27°$ $T_2 = ?$

Thus the temperature above which the tube will burst

$$= 900 - 273 = 627°\text{C}$$

PROBLEMS FOR PRACTICE

1. 500 ml of nitrogen at 27° C are cooled to —5°C at the same pressure. Calculate the new volume. [Ans. **446.7 ml]**
2. 400 ml of oxygen at 27°C were cooled to —15°C without the change in pressure. Calculate the contraction in volume. [Ans. **56.0 ml]**
3. A volume of hydrogen measures one cubic decimetre at 20°C and at a pressure of half an atmosphere. What will be its volume at 10°C and at 700 mm pressure ? [Ans. **0.524 dm^3]**
4. 300 litres of ammonia gas at 20°C and 20 atmosphere pressure are allowed to expand in a space of 600 litres capacity and to a pressure of one atmosphere. Calculate the drop in temperature. [Ans. **263.7 K]**
5. One litre flask containing vapours of methyl alcohol (Mol mass 32) at a pressure of 1 atm. and 25°C was evacuated till the final pressure was 10^{-3} mm. How many molecules of methyl alcohol were left in the flask ? [Ans. **3.24 × 10^{16} molecules]**
6. 28.32 litres of chlorine were liberated at normal conditions of temperature and pressure. Calculate the volume of the gas at 12°C and 780 mm pressure. [Ans. **28.80 litres]**
7. Temperature at the foot of a mountain is 30°C and pressure is 760 mm whereas at the top of the mountain these are 0°C and 710 mm. Compare the densities of the air at the foot and at the top of the mountain. [Ans. **0.964 : 1]**

HINTS FOR DIFFICULT PROBLEMS

4. $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ *i.e.* $\frac{20 \text{ atm} \times 300 \text{ L}}{293 \text{ K}} = \frac{1 \text{ atm} \times 600 \text{ L}}{T_2}$

or $T_2 = 29{\cdot}3$ K

Drop in temperature = 293—29·3 = 263·7 K

5. $P_1 = 10^{-3}$ mm, $V_1 = 1000$ cm^3, $T_1 = 298$ K

For converting this volume to volume at S.T.P., apply $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

i.e. $\frac{10^{-3} \times 1000}{298} = \frac{760 \times V_2}{273}$

or $V_2 = 1{\cdot}205 \times 10^{-3}$ cm^3

22400 cm^3 at S.T.P. ≡ $6{\cdot}02 \times 10^{23}$ molecules

$\therefore$ $1{\cdot}205 \times 10^{-3}$ cm^3 at S.T.P.

$$\equiv \frac{6{\cdot}02 \times 10^{23}}{22400} \times 1{\cdot}205 \times 10^{-3} \text{ molecules}$$

$$= 3{\cdot}24 \times 10^{16} \text{ molecules}$$

7. $d = \frac{PM}{RT}$. Hence $\frac{d_1}{d_2} = \frac{P_1}{T_1} \times \frac{T_2}{P_2}$

$$= \frac{760 \text{ mm}}{303 \text{ K}} \times \frac{273 \text{ K}}{710 \text{ mm}} = \frac{0{\cdot}964}{1}$$

TYPE II. Based on the equation PV = nRT

EXAMPLE 1. *Calculate the number of moles of hydrogen contained in 18 litres of the gas at 27°C and 70 cm pressure. Given that R = 0.0821 litre atm K^{-1} mol^{-1}. Further if the mass of hydrogen taken as above is found to be 1.350 g, calculate the molecular mass of hydrogen.*

Solution. Here we are given

$$V = 18 \text{ litres}$$
$$T = 27°C = 27 + 273 \text{ K} = 300\text{K}$$
$$P = 70 \text{ cm} = 70/76 \text{ atm}$$
$$R = 0.0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

Using the ideal gas equation,

$$PV = nRT$$

we have $n = \dfrac{PV}{RT} = \dfrac{(70/76)\ (18)}{(0\cdot0821)\ (300)}$

$= \mathbf{0\cdot67\ mole}$

Further we know that

$$n = \frac{\text{Mass}}{\text{Molecular mass}} = \frac{m}{M}$$

$$\therefore \quad M = \frac{m}{n} = \frac{1\cdot350}{0\cdot67} = \mathbf{2\cdot015\ u}$$

EXAMPLE 2. *10 g of O_2 were introduced into an evacuated vessel of 5 litre capacity maintained at 27°C. Calculate the pressure of the gas in atmospheres in the container.*

Solution. Since the volume of a gas is equal to the volume of its container, therefore

$$V = 5 \text{ litres}$$

Further, molecular mass of O_2 = 32·0, therefore the number of moles of O_2 gas are

$$n = \frac{10}{32} \text{ moles}$$

We are also given

$$T = 27°C = 27 + 273\text{K} = 300\text{K}$$

Taking R = 0·0821 litres atm K^{-1} mol^{-1} and using the ideal gas equation, PV = n RT we have

$$\mathbf{P} = \frac{n\,RT}{V} = \frac{(10/32)\ (0\cdot0821)\ (300)}{5}$$

$= \mathbf{1\cdot54\ atm.}$

- **EXAMPLE 3.** *Pressure of 1 g of an ideal gas A at 27°C is found to be 2 bar. When 2 g of another ideal gas B is introduced in the same flask at same temperature, the pressure becomes 3 bar. Find the relationship between their molecular masses.* **(N.C.E.R.T.)**

Solution. Suppose molecular masses of A and B are M_A and M_B respectively. Then their number of moles will be

$$n_A = \frac{1}{M_A}, \quad n_B = \frac{2}{M_B}$$

$P_A = 2$ bar, $P_A + P_B = 3$ bar *i.e.* $P_B = 1$ bar

Applying the relation PV = nRT

$$P_A V = n_A RT, \qquad P_B V = n_B RT$$

$$\therefore \quad \frac{P_A}{P_B} = \frac{n_A}{n_B} = \frac{1/M_A}{2/M_B} = \frac{M_B}{2\,M_A}$$

$$\text{or} \quad \frac{M_B}{M_A} = 2 \times \frac{P_A}{P_B} = 2 \times \frac{2}{1} = 4 \quad \text{or} \quad \mathbf{M_B = 4\,M_A}.$$

EXAMPLE 4. *340·5 mL of phosphorus vapour weigh 0·0625 g at 546°C and 0·1 bar pressure. What is the molar mass of phosphorus?* **(N.C.E.R.T.)**

Solution. *Step 1. Calculation of volume at 0°C and 1 bar pressure*

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \quad i.e. \quad \frac{0\cdot1 \times 340\cdot5}{546 + 273} = \frac{1 \times V_2}{273}$$

$$\text{or} \quad V_2 = 11\cdot35 \text{ mL}$$

11·35 mL of vapour at 0°C and 1 bar pressure weigh = 0·0625 g

∴ 22700 mL of vapour at 0°C and 1 bar pressure will weigh

$$= \frac{0\cdot0625}{11\cdot35} \times 22700 = 125 \text{ g}$$

∴ Molar mass = **125 g mol^{-1}**

Alternatively, using

$$R = 0\cdot083 \text{ bar dm}^3 \text{ K}^{-1} \text{ mol}^{-1}$$

$$PV = nRT \quad i.e. \quad n = \frac{PV}{RT}$$

$$= \frac{0\cdot1 \text{ bar} \times (340\cdot5 \times 10^{-3}\ dm^3)}{0\cdot083 \text{ bar dm}^3 \text{ K}^{-1} \text{ Mol}^{-1} \times 819 \text{ K}}$$

$$= 5 \times 10^{-4} \text{ mol}$$

$$\therefore \quad \text{Mass of 1 mole} = \frac{0\cdot0625}{5 \times 10^{-4}} \text{ g} = 125 \text{ g}$$

Molar mass = 125 g mol^{-1}

EXAMPLE 5. *8 g of methane is placed in 5 litre container at 27°C. Find Boyle constant.*

Solution. PV = Boyle constant

But $\quad PV = n\,RT = \dfrac{w}{M}RT$

$$= \frac{8}{16} \text{ mol} \times 0\cdot0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

$= \mathbf{12\cdot315\ L\ atm.}$

PROBLEMS FOR PRACTICE

1. Calculate the number of moles of hydrogen gas present in 500 cm^3 of the gas taken at 300K and 760 mm pressure. If this sample of hydrogen is found to have a mass equal to 4.09×10^{-2} g, calculate the molar mass of hydrogen.

   [Ans **2.03×10^{-2} mole. 2.01 g mol^{-1}**]

2. 2.802 g of N_2 gas is kept in a litre flask at 0°C. Calculate the pressure exerted by the gas.

   [Ans **2.24 atm**]

3. Calculate the molar volume of a gas at STP.

   [Ans **22.4 litres**]

4. A 500 ml sample of a gas weighs 0.326 g at 100°C and 0.500 atm. What is the molecular mass of the gas ?

   [Ans **39.9 amu**]

5. A large flask fitted with a stop-cock is evacuated and weighed ; its mass is found to be 134.567 g. It is then filled to a pressure of 735 mm at 31°C with a gas of unknown molecular mass and then reweighed ; its mass is 137.456 g. The flask is then filled with water and weighed again ; its mass is now 1067.9g. Assuming that the gas is ideal, calculate the molar mass of the gas.

   [Ans **80.25 g mol^{-1}**]

6. Calculate the temperature of 4·0 moles of a gas occupying 5 dm^3 at 3·32 bar (R = 0·083 bar dm^3 K^{-1} mol^{-1}) *(N.C.E.R.T.)* [Ans **50 K**]

7. Calculate the volume occupied by 8·8 g of CO_2 at 31·1°C and 1 bar pressure (R = 0·083 bar L K^{-1} mol^{-1}) *(N.C.E.R.T.)* [Ans **5·05 L**]

8. 2·9 g of a gas at 95°C occupied the same volume as 0·184 g of hydrogen at 17°C at the same pressure. What is the molar mass of the gas ?

   (N.C.E.R.T.) [Ans **40 g mol^{-1}**]

HINTS FOR DIFFICULT PROBLEMS

1. Proceed as in solved example 1.

2. 2·802 g of N_2 = 2·802/28 mol.

   Then apply PV = *n*RT

3. At S.T.P., P=1 atm, T=273 K. Apply PV=*n*RT.

   Take *n* = 1 mol, R = 0·0821 L atm K^{-1} mol^{-1}.

5. Mass of water filling the flask

   = (1067·9—134·567) *g* = 933·333 g

   ∴ Volume of flask = Volume of water filling the flask = 933·3 cm^3

   $(\because \text{density of } H_2O = 1 \text{ g cm}^{-3})$

   Now P = 735 mm, T = 31 + 273 K = 304 K,

   V = 933·3 cm^3

   Applying PV = *n*RT *i.e.* $\left(\frac{735}{760}\text{ atm}\right)\left(\frac{933\cdot3}{1000}L\right)$

   $= n \times 0\cdot0821 \text{ L atm K}^{-1}\text{ mol}^{-1} \times 304 \text{ K}$

   This gives *n* = 0·036 mol

   Mass of 0·036 mol of the gas

   = (137·456—134·567) g = 2·889 g

   ∴ Mass of 1 mol of the gas $= \frac{2\cdot889}{0\cdot036} = 80\cdot25$ g

6. PV = *n*RT

   or $T = \frac{PV}{nR} = \frac{3\cdot32 \times 5}{4\cdot0 \times 0\cdot083} = 50 \text{ K}$

7. Apply PV = *n*RT

8. As $P_1 = P_2$ and $V_1 = V_2$,

   $\therefore \quad n_1T_1 = n_2T_2$

   $$\frac{2\cdot9}{M_X} \times (95 + 273) = \frac{0\cdot184}{2} \times (17 + 273)$$

   or $M_X = \frac{2\cdot9 \times 368 \times 2}{0\cdot184 \times 290} = 40 \text{ g mol}^{-1}$

TYPE III. Based on the equation M = dRT/P

EXAMPLE 1 *The density of a gas is found to be 1.56 g/litre at 745 mm pressure and 65°C. Calculate the molecular mass of the gas.*

Solution. Here we have *d* = 1·56 g $litre^{-1}$

$$P = 745 \text{ mm} = \frac{745}{760} \text{ atm}$$

$$T = 65°C = 65 + 273 = 338 \text{ K}$$

$$R = 0\cdot0821 \text{ litre atm K}^{-1} \text{ mol}^{-1}$$

$$\therefore \quad M = \frac{dRT}{P} = \frac{1\cdot56 \times 0\cdot0821 \times 338}{745/760}$$

$$= \mathbf{44\cdot2 \ u}$$

EXAMPLE 2 *The density of a gas is 3·80 g L^{-1} at S.T.P. Calculate its density at 27°C and 700 torr pressure.*

Solution. $d = \frac{PM}{RT}$. For the same gas at two different pressures and temperatures,

$$\frac{d_1}{d_2} = \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$d_1 = 3\cdot80\ \mathrm{g\ L^{-1}}$, $P_1 = 760$ torr, $T_1 = 273$ K

$d_2 = ?$, $P_2 = 700$ torr, $T_2 = 300$ K

$$\therefore \quad \frac{3\cdot80}{d_2} = \frac{760}{700} \times \frac{300}{273} \text{ or } d_2 = 3\cdot185\ g\ \mathrm{L^{-1}}$$

EXAMPLE 3 *At 0°C, the density of a gaseous oxide at 2 bar is same as that of nitrogen at 5 bar. What is the molecular mass of the oxide ?* (N.C.E.R.T.)

Solution. Using the solution, $d = \frac{MP}{RT}$, at the same temperature

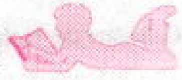
$$\underset{\text{(Gaseous oxide)}}{M_1P_1} = \underset{(N_2)}{M_2P_2} \quad \text{(as R is constant)}$$

$$\therefore \quad M_1 \times 2 = 28 \times 5$$

(Molecular mass of $N_2 = 28\,u$)

or $\quad M_1 = 70\,u$

PROBLEMS FOR PRACTICE



1. The density of a gas is found to be 3.43 g/litre at 300K and 1.00 atm pressure. Calculate the molar mass of the gas. [84.5 g mol^{-1}]
2. If the density of a gas at the sea level at 0°C is 1·29 kg m^{-3}, what will be its molar mass (Assume that pressure is equal to 1 bar). [29·3 g mol^{-1}]
3. Density of a gas is found to be 5·46 g/dm^3 at 27°C and at 2 bar pressure. What will be its density at STP ? *(N.C.E.R.T.)* [3 g/dm^3]

HINTS FOR DIFFICULT PROBLEMS

2. $M = \frac{dRT}{P} = \frac{1\cdot29\ \mathrm{kg\ m^{-3}} \times 8\cdot314\ \mathrm{Nm\ K^{-1}\ mol^{-1}} \times 273\ \mathrm{K}}{1\cdot0 \times 10^5\ \mathrm{N\ m^{-2}}} = 0\cdot0293\ \mathrm{kg\ mol^{-1}} = 29\cdot3\ \mathrm{g\ mol^{-1}}$ (1J=1 Nm)

(4) DALTON'S LAW OF PARTIAL PRESSURES

The various gas laws discussed so far dealt only with the pressure, volume and temperature of a single gas. However, if two or more chemically non-reacting gases are enclosed in the same vessel, the pressures exerted by the mixtures were first studied by John Dalton in 1807. He put forward the following result known after him as Dalton's law of partial pressures :

If two or more gases which do not react chemically are enclosed in a vessel, the total pressure exerted by the gaseous mixture is equal to the sum of all the partial pressures that each gas would exert when present alone in the same vessel at the same temperature.

The term partial pressure of a particular gas in a gaseous mixture enclosed in a given space implies the pressure which that gas would exert when present alone in the same space at the same temperature. Let $p_1, p_2, p_3 \cdots p_n$ be the partial pressures of n gases enclosed in a given vessel and P be the total pressure of the gaseous mixture. Then by Dalton's Law of Partial Pressures, we have

$$\boxed{P = p_1 + p_2 + p_3 + \ldots p_n}$$

Suppose we enclose '*a*' moles of hydrogen in a vessel at a given temperature and let its pressure be 50 mm of Hg. Now enclose '*b*' moles of oxygen in the same vessel at the same temperature. Let its pressure be 100 mm. Now if the same quantities of the two gases are enclosed in the same vessel at the same temperature, the total pressure exerted by the gaseous mixture would be 150 mm as shown in Fig. 2.13 in accordance with the Dalton's Law of Partial Pressures.

$$P_{H_2} = 50\ \text{mm},\ P_{O_2} = 100\ \text{mm},$$

$$P = P_{H_2} + P_{O_2} = 150\ \text{mm}$$

Applications of Dalton's Law of Partial Pressures.

(i) In the determination of pressure of a dry gas. Whenever a gas is collected over water, it is moist, *i.e.* it is saturated with water vapours which exert their own pressure. The pressure due to water vapours is called *aqueous tension*.

When the volume of the gas is measured after careful levelling (so that the level inside the measur-

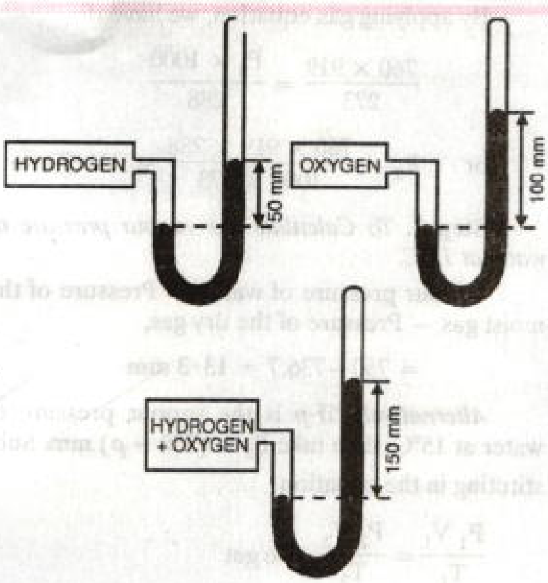


FIGURE 2.13. Illustration of Dalton's Law of Partial Pressures.

ing tube and outside in the jar are same) the total pressure exerted by the gas and the water vapours is equal to the atmospheric pressure as shown in Fig. 2.14.

If P and P′ are the pressure of the dry gas and the moist gas respectively at t°C and p is the aqueous tension at that temperature, then by *Dalton's Law of Partial Pressures*

$$P = P' - p$$

or $P_{\text{dry gas}} = P_{\text{moist gas}}$ – Aqueous tension (at t°C).

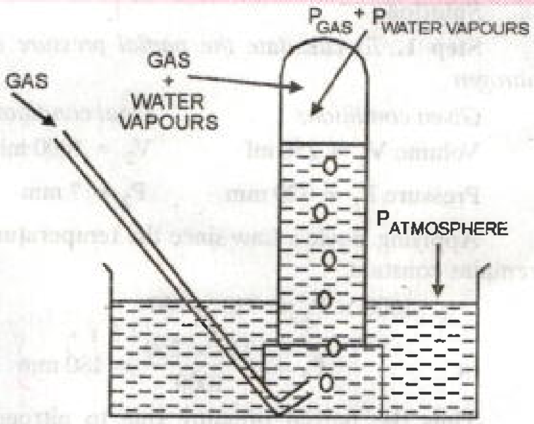


FIGURE 2.14. $P_{gas} + P_{water\ vapours} = P_{moist\ gas}$

***(ii)* In the calculation of partial pressures.** In a mixture of non-reacting gases A, B, C etc., if each gas is considered to be an ideal gas, then applying PV = nRT,

$$p_A = n_A\frac{RT}{V}, p_B = n_B\frac{RT}{V}, p_C = n_C\frac{RT}{V}$$

and so on.

By Dalton's law of partial pressures,

$$\text{Total pressure, } P = p_A + p_B + p_C + \ldots$$

$$= \frac{RT}{V}(n_A + n_B + n_C + \ldots)$$

$$\therefore \quad \frac{p_A}{P} = \frac{n_A}{n_A + n_B + n_C + \ldots} = x_A$$

(mole fraction of A)

or $p_A = x_A \times P$.

Similarly, $p_B = x_B \times P$ and so on. Thus

Partial pressure of A = Mole fraction of A × Total pressure

NUMERICAL PROBLEMS ON LAW OF PARTIAL PRESSURES

EXAMPLE 1. *38.00 ml of moist nitrogen gas were collected at 27°C and 746.5 mm pressure. Calculate the volume of the gas at 0°C and 760 mm pressure. (Aq. tension at 27°C is 26.5 mm).*

Solution.

Given conditions	*Final conditions*
$V_1 = 38.0$ ml	$V_2 = ?$ ml
$P_1 = 746.5 - 26.5 = 720$ mm	$P_2 = 760$ mm
$T_1 = 27 + 273 = 300$K	$T_2 = 0 + 273 = 273$K

By applying the general gas equation :

$$\frac{760 \times V_2}{273} = \frac{720 \times 38}{300}$$

$$\therefore \quad V_2 = \frac{720 \times 38}{300} \times \frac{273}{760} = 32{\cdot}76 \text{ ml}$$

Volume of nitrogen at 0°C and 760 mm pressure = **32·76 ml.**

EXAMPLE 2. *250 ml of nitrogen maintained at 720 mm pressure and 380 ml of oxygen maintained at 650 mm pressure are put together in one litre flask. If the temeprature is kept constant, what will be the final pressure of the mixture ?*

Solution.

Step 1. *To calculate the partial pressure of nitrogen*

Given conditions	*Final conditions*
Volume $V_1 = 250$ ml	$V_2 = 1000$ ml
Pressure $P_1 = 720$ mm	$P_2 = ?$ mm

Applying Boyle's Law since the temperature remains constant

$$1000 \times P_2 = 720 \times 250$$

or $$P_2 = \frac{720 \times 250}{1000} = 180 \text{ mm}$$

Thus the partial pressure due to nitrogen $(p_{N_2}) = 180$ mm.

Step 2. *To calculate the partial pressure of oxygen*

Given conditions	*Final conditions*
$V_1 = 380$ ml	$V_2 = 1000$ ml
$P_1 = 650$ mm	$P_2 = ?$ mm

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

$$1000 \times P_2 = 380 \times 650$$

or $$P_2 = \frac{380 \times 650}{1000} = 247 \text{ mm}$$

Thus, the partial pressure due to oxygen (p_{O_2}) = 247 mm.

Step 3. *To calculate the final pressure of the gaseous mixture.*

If P is the final pressure of the gaseous mixture, then according to Dalton's Law of Partial Pressures, $P = P_{N_2} + P_{O_2} = 180 + 247 = \mathbf{427}$ **mm.**

EXAMPLE 3. *A given mass of a gas occupies 919.0 ml in dry state at STP. The same mass when collected over water at 15°C and 750 mm pressure occupies one litre volume. Calculate the vapour pressure of water at 15°C.*

Solution.

Step 1. *To calculate the pressure of the dry gas at 15°C and 750 mm pressure using the gas equation.*

Given conditions at STP	*Final conditions*
$V_1 = 919$ ml	$V_2 = 1000$ ml
$P_1 = 760$ mm	$P_2 = ?$ (Dry state)
$T_1 = 273$ K,	$T_2 = 273 + 15 = 288$K

By applying gas equation, we have

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

or $$P_2 = \frac{760 \times 919 \times 288}{1000 \times 273} = 736 \cdot 7 \text{ mm}$$

Step 2. *To Calculate the vapour pressure of water at 15°C.*

Vapour pressure of water = Pressure of the moist gas − Pressure of the dry gas,

$$= 750 - 736.7 = \mathbf{13 \cdot 3 \text{ mm}}$$

Alternatively, if p is the vapour pressure of water at 15°C, then take $P_2 = (750 - p)$ mm. Substituting in the equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ we get}$$

$$\frac{760 \times 919}{273} = \frac{(750 - p) \times 1000}{288}. \text{ Solve for } p.$$

EXAMPLE 4. *A 2-L flask contains 1·6 g of methane and 0·5 g of hydrogen at 27°C. Calculate the partial pressure of each gas in the mixture and hence calculate the total pressure.*

Solution. $1 \cdot 6\,g\,CH_4 = \frac{1 \cdot 6}{16}$ mole $= 0 \cdot 1$ mole.

Partial pressure of CH_4 (p_{CH_4})

$$= n_{CH_4} \times \frac{RT}{V}$$

$$= \frac{0 \cdot 1 \times 0 \cdot 0821 \times 300}{2} = \mathbf{1 \cdot 23 \text{ atm}}$$

$$0 \cdot 5\,g\,H_2 = \frac{0 \cdot 5}{2} \text{ mole} = 0 \cdot 25 \text{ mole}$$

Partial pressure of H_2 $(p_{H_2}) = n_{H_2} \times \frac{RT}{V}$

$$= \frac{0 \cdot 25 \times 0 \cdot 0821 \times 300}{2} = \mathbf{3 \cdot 079 \text{ atm}}$$

Total pressure $= p_{CH_4} + p_{H_2}$

$$= 1 \cdot 23 + 3 \cdot 079 = \mathbf{4 \cdot 31 \text{ atm}}$$

EXAMPLE 5. *A gaseous mixture contains 56 g N_2, 44 g CO_2 and 16 g CH_4. The total pressure of the mixture is 720 mm Hg. What is the partial pressure of CH_4 ?*

Solution. $56\ g\ N_2 = \frac{58}{28} = 2$ mole,

$$44\ g\ CO_2 = \frac{44}{44} = 1 \text{ mole},$$

$$16\ g\ CH_4 = \frac{16}{16} = 1 \text{ mole}$$

Partial pressure of CH_4

$$= \frac{n_{CH_4}}{n_{N_2} + n_{CO_2} + n_{CH_4}} \times P$$

$$= \frac{1}{2+1+1} \times 720 = \mathbf{180\ mm}$$

PROBLEMS FOR PRACTICE

1. 200 ml of hydrogen and 250 ml of nitrogen each measured at 15°C and 760 mm pressure are put together in a 500 ml flask. What will be the final pressure of the mixture at 15°C ? **[Ans. 684 mm]**
2. 400 ml of N_2 gas at 700 mm and 300 ml of H_2 gas at 800 mm were introduced into a vessel of 2 litres at the same temperature. Calculate the final pressure of the gas mixture. **[Ans. 260 mm]**
3. Two vessels of capacities 1.5 litres and 2.0 litres containing hydrogen at 750 mm pressure and oxygen at 100 mm pressure respectively are connected to each other through a valve. What will be the final pressure of the gaseous mixture assuming that temperature remains constant ? **[Ans. P_{H_2} = 321.43 mm. P_{O_2} = 57.14 mm. $P_{mixture}$ = 378.57 mm]**
4. What will be the pressure exerted by a mixture of 3·2 g of methane and 4·4 g of carbon dioxide contained in a 9 dm^3 flask at 27°C ? *(N.C.E.R.T.)* **[Ans. 0·82 atm]**
5. What will be the pressure of the gas mixture when 0·5 L of H_2 at 0·8 bar and 2·0 L of oxygen at 0·7 bar are introduced in a 1 L vessel at 27°C ? *(N.C.E.R.T.)* **[Ans. 0·4 + 1·4 = 1·8 bar]**
6. 8 g of oxygen and 4 g of hydrogen are confined in a vessel of 1 dm^3 at 27°C. Calculate the total pressure of the mixture ($R = 0{\cdot}083$ bar $dm^3\ K^{-1}\ mol^{-1}$) *(N.C.E.R.T.)*
7. A mixture of hydrogen and oxygen at one bar pressure contains 20% by weight of hydrogen. Calculate the partial pressure of hydrogen. *(N.C.E.R.T.)* **[Ans. 0·8 bar]**

HINTS FOR DIFFICULT PROBLEMS

1. As temperature is kept constant at 15°C, for calculation of partial pressure of H_2 gas,

$$P_1V_1 = P_2V_2$$

i.e. $200 \times 760 = P_2 \times 500$ *i.e.* $p_{H_2} = 304$ mm

For calculation of partial pressure of N_2,

$$P_1'V_1' = P_2'V_2'$$

i.e. $760 \times 250 = P_2' \times 500$ *i.e.* $p_{N_2} = 380$ mm

$\therefore$ Final pressure of the mixture

$$= 304 + 380 = 684 \text{ mm}$$

3. Final volume = 1·5 L + 2·0 L = 3·5 L

For partial pressure of H_2, $P_1V_1 = P_2V_2$

i.e. $750 \times 1{\cdot}5 = P_2 \times 3{\cdot}5$

or $p_{H_2} = (750 \times 1{\cdot}5) / 3{\cdot}5 = 321{\cdot}43$ mm

For partial pressure of O_2, $P_1'V_1' = P_2'V_2'$

i.e. $100 \times 2 = P_2' \times 3{\cdot}5$

or $p_{O_2} = (100 \times 2) / 3{\cdot}5 = 57{\cdot}14$ mm

$\therefore P_{mixture} = 321{\cdot}43 + 57{\cdot}14 \text{ mm} = 378{\cdot}57$ mm

4. $p = \frac{n}{V}RT = \frac{w}{M}\frac{RT}{V}$

p_{CH_4}

$$= \left(\frac{3{\cdot}2}{16}\text{ mol}\right)\frac{0{\cdot}0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 300\ K}{9\ dm^3}$$

$= 0{\cdot}55$ atm

p_{CO_2}

$$= \left(\frac{4{\cdot}4}{44}\text{ mol}\right)\frac{0{\cdot}0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 300\ K}{9\ dm^3}$$

$= 0{\cdot}27$ atm

$$p_{Total} = 0{\cdot}55 + 0{\cdot}27$$

$$= 0{\cdot}82 \text{ atm}$$

5. Similar to Problem 1 and Problem 2.

7. $p_{H_2} = \frac{n_{H_2}}{n_{H_2} + n_{O_2}} \times P$

$$= \frac{20\,w/2}{20\,w/2 + 80\,w/32} \times 1 \text{ bar}$$

$$= \frac{10}{10 + 2{\cdot}5} = 0{\cdot}8 \text{ bar}$$

(5) GRAHAM'S LAW OF DIFFUSION/EFFUSION

When we enter into kitchen, we get the smell of food. Similarly, if a student in a class-room has used perfume, everybody in the room gets the fragrance of the perfume. This is because the molecules of the aroma of the food or the perfume mix with the air. *The spreading of the molecules of a gas throughout the available space is called* **diffusion.** It differs form the term **effusion** *which is a process in which a gas under pressure escapes out of a fine hole or orifice in a vessel e.g.* leaking out of a gas from a cylinder or air from a punctured tyre or escaping out of perfume molecules through the atomizer etc. However, the process of effusion is always followed by the process of diffusion.

Thomas Graham studied the rates of diffusion of different gases. He observed that the lighter gased diffuse faster than the denser gases. In 1831, he put forward the following law :

Under similar conditions of temperature and pressure, the rates of diffusion/effusion of different gases are inversely proportional to the square root of their densities.

For two gases having densities d_1 and d_2 and rates of diffusion r_1 and r_2 under similar conditions of temperature and pressure

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

Here the term 'Rate of effusion diffusion' implies as under :

Rate of effusion/diffusion

$$= \frac{\text{Volume of the gas effused/diffused}}{\text{Time taken}}$$

The law may be modified for different types of calculations as follows :

(*i*) *Calculation of molecular masses.* As density is mass per ml of the gas and vapour density is mass of 11200 ml of the gas at S.T.P., therefore ratio of densities of two gases is equal to the ratio of their vapour densities.

As mol. mass = 2 × vapour density, we can also write

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

where M_1 and M_2 are the molecular masses of the two gases.

Thus knowing the relative rates of effusion of the two gases and knowing the molecular mass of one of them, that of the other can be calculated.

If two gases are taken at different pressures, then as greater the pressure, greater is the number of molecules hitting per unit area, greater is the rate of diffusion. In such cases, Graham's law of diffusion can be written as

$$\frac{r_1}{r_2} = \frac{P_1}{P_2}\sqrt{\frac{d_2}{d_1}} = \frac{P_1}{P_2}\sqrt{\frac{M_2}{M_1}}$$

(*ii*) *Comparison of volumes of two different gases effused/diffused in the same time.* Suppose v_1 is the volume of gas 1 diffused in time t and v_2 is the volume of gas 2 diffused in the same time t under the same conditions of teperature and pressure and through the same orifice. Then

$$\text{Rate of diffusion of gas 1 } (r_1) = \frac{v_1}{t}$$

$$\text{Rate of diffusion of gas 2 } (r_2) = \frac{v_2}{t}$$

If d_1 and d_2 are their respective densities or M_1 and M_2 are their respective molecular masses, then

$$\frac{r_1}{r_2} = \frac{v_1/t}{v_2/t} = \frac{v_1}{v_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Thus volumes of two gases effused/diffused in the same time (through the same orifice) under similar conditions of temperature and pressure are inversely proportional to the square roots of their densities.

(*iii*) *Comparison of times taken for effusion/diffusion of the same volume of two different gases.* Suppose t_1 is the time taken for the gas 1 for diffusion of volume v and t_2 is the time taken for gas 2 for diffusion of the same volume v under same conditions of temperature and pressure and through the same orifice. Then

$$\frac{r_1}{r_2} = \frac{v/t_1}{v/t_2} = \frac{t_2}{t_1} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

Thus *times taken for effusion/diffusion of same volume of two different gases under the same conditions of temperature and pressure (through the same orifice) are directly proportional to the square roots of their densities.*

NUMERICAL PROBLEMS ON LAW OF PARTIAL PRESSURES

EXAMPLE 1. *Equal volumes of two gases A and B diffuse through a porous pot in 20 and 10 seconds respectively. If the molar mass of A is 80, calculate the molar mass of B.* **(N.C.E.R.T.)**

Solution. Suppose the volume of each gas diffused = v cc. Then by Graham's law of diffusion

$$\frac{r_A}{r_B} = \frac{v/20}{v/10} = \sqrt{\frac{M_B}{M_A}}$$

$$\text{or} \quad \frac{1}{2} = \sqrt{\frac{M_B}{80}}$$

$$\text{or} \quad \mathbf{M_B = 20\ g\ mol^{-1}}$$

EXAMPLE 2. *127 ml of a certain gas diffuse in the same time as 100 ml of chlorine under the same conditions. Calculate the molecular mass of the gas.*

Solution. If t is the time taken for diffusion of each gas, then by Graham's law of diffusion

$$\frac{r_X}{r_{Cl_2}} = \frac{127/t}{100/t} = \sqrt{\frac{M_{Cl_2}}{M_X}} = \sqrt{\frac{71}{M_X}}$$

$$\text{or} \quad \frac{71}{M_X} = \left(\frac{127}{100}\right)^2 \quad \text{or} \quad \mathbf{M_X = 44\ u}$$

EXAMPLE 3. *Through the two ends of a glass tube of length 200 cm, hydrogen chloride gas and ammonia are allowed to enter. At what distance ammonium chloride will first appear ?* **(N.C.E.R.T.)**

Solution. By Graham's law of diffusion

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}} = \sqrt{\frac{36\cdot5}{17}} = \sqrt{2\cdot147}$$

$$= 1\cdot465.$$

Thus NH_3 travels 1·465 times faster than HCl. In other words, NH_3 will travel 1·465 cm in the same time in which HCl travels 1 cm.

Length of the tube = 200 cm.

∴ Distance travelled in the tube by

$$NH_3 = \frac{1\cdot465}{1\cdot465 + 1} \times 200 = 118\cdot9\ \text{cm}$$

Thus NH_4Cl will first appear at a distance of 118·9 cm from NH_3 end or 81·1 cm from HCl end.

PROBLEMS FOR PRACTICE

1. Calculate the molar mass of an unknown gas which diffuses 1·117 times faster than oxygen gas through the same aperture under the same conditions of temperature and pressure. [Ans. **25·65 g mol^{-1}**]
2. If 25 ml of CO_2 diffuses out of a vessel in 75 seconds, what volume of SO_2 would diffuse out in the same time under the same conditions ? [Ans. **20·73 ml**]
3. Uranium isotopes have been separated by taking advantage of the different rates of diffusion of the two forms of uranium hexafluoride, one containing U—238 isotope and the other containing U—235. What are the relative rates of diffusion of these two molecules under ideal conditions ? [Ans. **0·9957 : 1·0**]
4. 50 ml of hydrogen takes 10 minutes to diffuses out of a vessel. How long will 40 ml of oxygen take to diffuse out under similar conditions ? [Ans. **32 minutes**]
5. A small quantity of gaseous NH_3 and HBr are introduced simultaneously into the opposite ends of an open tube which is one metre long. Calculate the distance of the white solid NH_4Br formed from the end which was used to introduce NH_3. [Ans. **68·58 cm**]

HINTS FOR DIFFICULT PROBLEMS

1. $\dfrac{r_X}{r_{O_2}} = \sqrt{\dfrac{M_{O_2}}{M_X}}$ or $1\cdot117 = \sqrt{\dfrac{32}{M_X}}$

   or $M_X = \dfrac{32}{(1\cdot117)^2} = 25\cdot65\ g\ mol^{-1}$

2. $\dfrac{r_1}{r_2} = \dfrac{v_1/t_1}{v_2/t_2} = \sqrt{\dfrac{M_2}{M_1}}$

   or $\dfrac{25/75}{v_2/75} = \sqrt{\dfrac{64}{44}}$

HINTS CONTD.

or $\frac{25}{v_2} = \sqrt{\frac{64}{44}}$ or $v_2 = 20{\cdot}73$ ml

3. $\frac{r\,(^{238}UF_6)}{r\,(^{235}UF_6)} = \sqrt{\frac{M\,(^{235}UF_5)}{M\,(^{238}UF_6)}}$

$= \sqrt{\frac{235 + 19 \times 6}{238 + 19 \times 6}} = \sqrt{\frac{349}{352}} = 0{\cdot}9957 : 1$

4. $\frac{r_{H_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{H_2}}}$ *i.e.* $\frac{50/10}{40/t} = \sqrt{\frac{32}{2}}$

or $\frac{5t}{40} = 4$

or $t = 32$ min.

5. Similar to solved example 3.

For more numericals, see 'C.B.S.E. (P.M.T.) and I.I.T. (Mains)' at the end of this unit. Problems 11 and 12, page 2/60 and Problems 10, 13 and 15, page 2/65, 66.

ADD TO YOUR KNOWLEDGE

1. **Volume coefficient (α_v).** At constant pressure, the increase in volume of a gas per degree rise of temperature per cc of the gas at 0°C is called the volume coefficient of the gas. Mathematically, $\alpha_v = \frac{V_t - V_0}{V_0 \times t}$

   V_0 = volume of the gas at 0°C

   V_t = volume of the gas at t°C

   For all gases, value of α_v is 1/273.

2. **Pressure coefficient (α_P).** At constant volume, the increase in the pressure of a gas per degree rise of temperature divided by its pressure at 0°C is called pressure coefficient of the gas. Mathematically

   $$\alpha_P = \frac{P_t - P_0}{P_0 \times t}$$

   For all gases, value of α_P is 1/273.

3. **Boltzmann constant (k)** = Gas constant per molecule $= \frac{R}{N_0} = \frac{8{\cdot}314\ JK^{-1}\ mol^{-1}}{6{\cdot}02 \times 10^{23}\ \text{molecules}\ mol^{-1}}$

   $= 1{\cdot}38 \times 10^{-23}\ JK^{-1}\ \text{molecule}^{-1}$.

4. Gases having the same molecular masses have same rates of diffusion *e.g.* CO, N_2, C_2H_4, B_2H_6 (mol mass = 28).

5. **Atmolysis.** The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities is called atmolysis. It has been applied with success for the separation of isotopes and other gaseous mixtures.

2.5. Kinetic Molecular Theory of Gases

The general properties of gases such as expansibility, compressibility, liquefaction, low densities, diffusion or effusion etc. have been observed experimentally. Similarly, various gas laws such as Boyle's law, Charles's law etc. have been obtained on the basis of experimental studies. To explain these general properties of the gases and the gas laws theoretically, various workers, from time to time, have tried to give a theoretical model of the gas. The first such model was put forward by Bernoulli in 1738 and later improved upon by various workers. Finally in the complete form, it has been put forward by Clausius in 1857 and is known as 'Kinetic-molecular theory of gases'. It was so called because it assumes the gas to be made up of a large number of molecules which were in ceaseless motion. For the same reason, it is also called a 'Dynamic particle model' of the gas. The name 'Microscopic model' is also used because the model assumes the gas to be made up of molecules which cannot be seen.

Postulates or Assumptions of Kinetic Theory of Gases – The Microscopic Model of a Gas. The main assumptions on which the kinetic theory of gases is based are as follows :

(*i*) *Every gas is made up of a large number of extremely small particles called molecules. All the molecules of a particular gas are identical in mass and size and differ in these from gas to gas.*

(*ii*) *The molecules of a gas are separated from each other by large distances so that the actual volume of the molecules is negligible as compared to the total volume of the gas.*

(*iii*) *The distances of separation between the molecules are so large that the forces of attraction or repulsion between them are negligible.*

(*iv*) *The force of gravitation on the molecules is also supposed to be negligible.*

(*v*) *The molecules are supposed to be moving continuously in different directions with different velocities. Hence they keep on colliding with one another (called molecular collisions) as well as on the walls of the containing vessel.*

(*vi*) *The pressure exerted on the walls of the containing vessel is due to the bombardment of the molecules on the walls of the containing vessel.*

(*vii*) *The molecules are supposed to be perfectly elastic hard spheres so that no energy is wasted when the molecules collide with one another or with the walls of the vessel. The energy may, however, be transferred from some molecules to the other on collision.*

(*viii*) *Since the molecules are moving with different velocities, they possess different kinetic energies. However, the average kinetic energy of the molecules of a gas is directly proportional to the absolute temperature of the gas.*

Justification of the above postulates :

Postulates (i) and (ii) are easily justified from the fact that when a certain mass of water at 100°C changes into steam at the same temperature, the volume of steam is nearly 1600 times greater than the volume of water. Thus, the same number of water molecules have spread over a much larger space. Further, gases can be compressed. Both these experiments support the view that a gas must be made up of extremely small particles (called molecules) separated from each other by large distances.

Postulate (*iii*) is supported by a simple observation that even a highly compressed gas expands when the pressure on it is decreased. This would not have been possible if strong forces of attraction existed between the molecules.

Postulate (*iv*) can be seen to be correct on the basis that if a cylinder filled with air is inverted over another cylinder containing a heavier gas (heavier than air) like bromine, even such a heavier gas travels up into the cylinder filled with air.

Postulate (*v*) is borne out by the observation that when a beam of light enters a dark room (*e.g.* from a projector in a cinema hall) the dust particles that fall into the path of the beam of light are seen to be in constant motion. Obviously, this must be due to the hitting of the dust particles by the air molecules which themselves in turn must be in motion. When the molecules move, they will naturally collide. The fact that a gas fills up a vessel of any size in a very short time further supports this postulate.

Postulate (*vi*) is quite obvious. Since the molecules are continuously moving, they can collide not only with one another but also with the walls of the container. Since a large number of molecules are hitting the wall, they will exert some significant push or an outward force on the wall. The force exerted on a unit area of the wall is called the pressure. This concept is further supported by the inflation of a rubber balloon or a cycle tube when more and more air is pumped into it.

Postulate (vii) states that the collisions are perfectly elastic. If it were not so, the forces of friction would have slowed down the molecules during every collision. Ultimately, the gas should have settled down after some time. Since this, in fact, does not happen, the postulate must be correct.

Postulate (*viii*) has emerged as a result of the fact that when the temperature of a gas is raised, the molecules start moving faster (as observed by the increase of pressure). In other words, their individual velocities increase and hence the kinetic energy increases. On the contrary, when a gas is cooled, the molecules slow down and hence the kinetic energy decreases. The liquefaction of gas clearly supports this view.

2.6. Maxwell's Distribution of Molecular Speeds/Energies

At a particular temperature, the different molecules of a gas possess different speeds. Further due to continuous collisions of the molecules among themselves as well as against the walls of the container, their speeds keep on changing. Maxwell and Boltzmann, however, showed that as a result of collisions, though some molecules are speeded up, some others are slowed down and hence the fractions of molecules possessing particular speed remains constant at constant temperature. This is called Maxwell-Boltzmann distribution and is shown by the curves in Fig. 2.15(*a*) for two different temperatures.

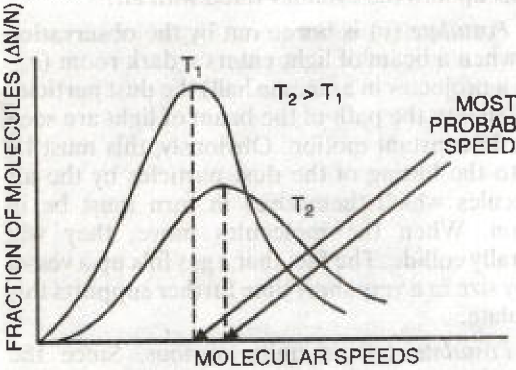


FIGURE 2.15(a). Maxwell's distribution of speeds at two different temperatures.

The peak of the curve corresponds to *a speed possessed by the maximum fraction of the molecules* and is called the **most probable speed.** We observe that with rise in temperature, the most probable speed increases. This is expected because with rise in temperature, the average speed of the gas molecules increases. However, it may be noted that the fraction of molecules possessing most probable speed decreases with increase in temperature.

2.7. Kinetic Gas equation

On the basis of the various assumptions made in the kinetic theory of gases, a mathematical equation has been derived from which all the gas laws can be deduced. This equation is known as 'kinetic gas equation.' It is usually written in the form

$$PV = \frac{1}{3} mnu^2$$

where P = Pressure exerted by the gas,

V = Volume of the gas

m = Mass of each molecule of the gas

n = Total number of molecules present in volume V

u = Root Mean Square speed of the gas

For 1 mole, $m \times n$ = mass of 1 mole = M, molar mass in g. Hence $PV = \frac{1}{3} Mu^2$ or

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

where $d = M/V$ is density of the gas

Types of speeds. *It may be noted that there are three types of speeds of gaseous molecules which are commonly used.* These are

(*i*) **Most probable speed (α).** *This is the speed possessed by the maximum fraction of molecules.*

(*ii*) **Root Mean Square (RMS) speed (u).** *It is the square root of the mean of the squares of the speeds of the molecules. Thus if $v_1, v_2, v_3 .... v_n$ are the speeds of n molecules then*

Root Mean Square speed (u)

$$= \sqrt{\frac{v_1^2 + v_2^2 + \ ... + v_n^2}{n}}$$

(*iii*) **Average speed (v).** *It is the average of the different speeds of all the molecules.*

$$\textit{Average speed}\ (v) = \frac{v_1 + v_2 + ... + v_n}{n}$$

Note. Instead of symbols, α, v and u, symbols u_{mp}, u_{av} and u_{rms} are often used.

Relationship between different types of speeds. As derived above, for root mean square speed

$$u = \sqrt{\frac{3\,RT}{M}}$$

Similarly, for most probable speed (α) and average speed (v), we have

$$\alpha = \sqrt{\frac{2\,RT}{M}}, \quad v = \sqrt{\frac{8\,RT}{\pi M}}$$

Thus the three types of speeds are related to each other as

$$\boxed{\begin{gathered} v = 0{\cdot}921\,u\,, \ \alpha = 0{\cdot}816\,u \\ \alpha : v : u = 1 : 1{\cdot}128 : 1{\cdot}224 \end{gathered}}$$

These may be represented graphically in the Maxwell distribution curve for speeds as follows :

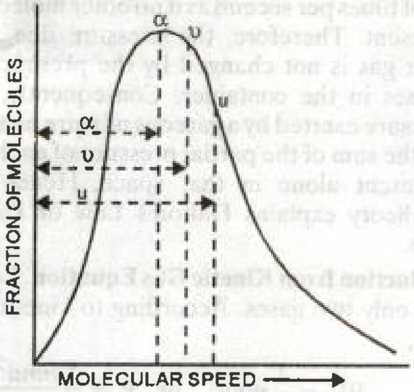


FIGURE 2.15(b). Representation of relative values of α , υ and u.

2.8. Explanation/deduction of Gas Laws from Kinetic Theory

(1) Boyle's Law

Explanation on the Basis of Kinetic Theory. According to Kinetic theory of gases, at constant temperature, the average kinetic energy and hence the average speed of the molecules is constant. Further, the number of molecules present in a given mass of a gas is also constant.

Let the volume of a given mass of a gas be reduced to one half of its original volume. The same number of molecules with their same average speed will now have half the original space to move about. As a result, the number of molecules striking the unit area of the walls of the container in a given time will get doubled and consequently the pressure is also doubled. Conversely, if the volume of a given mass of a gas is doubled at constant temperature (Fig. 2.16) the same number of molecules with their same average speed will now have double the space to move about. Consequently, the number of molecules striking the unit area of the walls of the container in a given time will now become one half the original number. As a result, the pressure of the gas will be reduced to one half of its original value. Thus it is obvious from the above discussion that pressure increases accordingly as the volume decreases or vice versa at constant temperature. This statement represents nothing else but Boyle's Law.

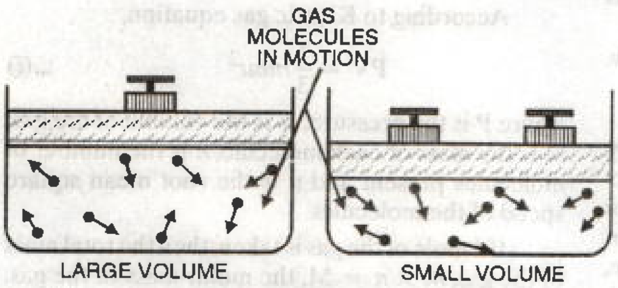


FIGURE 2.16. Rate of molecular collisions increases by decrease in volume.

Deduction from Kinetic Gas Equation. According to kinetic gas equation

$$PV = \frac{1}{3} mnu^2$$

$$= \frac{2}{3} \cdot \frac{1}{2} mnu^2 = \frac{2}{3} \cdot \frac{1}{2} Mu^2$$

(where $m \times n = M$ is the total mass of the gas)

But $\frac{1}{2} Mu^2$ = Kinetic energy of the gas

$$\therefore \quad PV = \frac{2}{3} K.E. \qquad ...(i)$$

Further, according to one of the postulates of the kinetic theory of gases,

$$K.E. \propto \text{Absolute Temperature (T)}$$

$$\text{or} \quad K.E. = kT \qquad ...(ii)$$

where k is a constant of proportionality.

Putting this value in equation (*i*), we get

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

As $\frac{2}{3}$ is a constant quantity, k is also a constant, therefore, if T is kept constant, $\frac{2}{3} kT$ will be constant. Hence PV = constant, if T is kept constant, which is Boyle's law.

(2) Charles' Law

Explanation on the Basis of Kinetic Theory. According to the kinetic theory of gases, the average kinetic energy and hence the average speed of the gas molecules is directly proportional to its absolute temperature. Thus, it follows that when the temperature of a gas is increased at constant volume, the average kinetic energy of its molecules increases and hence the molecules would move faster (Fig. 2.17). As a result, the molecules of the gas will strike the unit area of the walls of the container more frequently and vigorously. Consequently, the pressure of the gas will increase accordingly. Thus, at constant volume, the pressure of a gas increases with rise in temperature. This explains the Pressure Law.

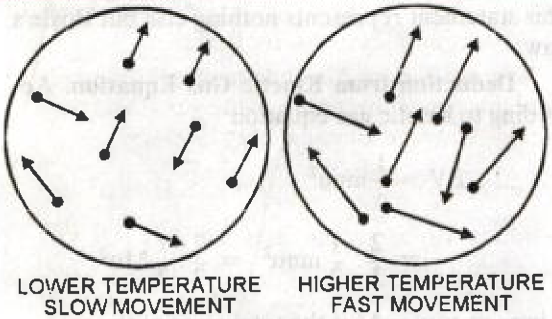


FIGURE 2.17.

On the other hand, if the pressure of the gas is to be maintained constant, the force per unit area on the walls of the container in a given time must be kept the same. This can, however, be achieved by increasing the volume proportionately. Thus, at constant pressure, the volume of a given mass of a gas increases with increase in temperature. This explains Charles' Law.

Deduction from Kinetic Gas Equation. As deduced in equation (*ii*) above from the kinetic gas equation, we have

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

This may be rewritten as $\frac{V}{T} = \frac{2}{3}\frac{k}{P}$

$\frac{2}{3}$ is constant, k is also constant, hence if P is kept constant, $\frac{V}{T}$ = constant. which is Charles' law.

(3) Dalton's Law of Partial Pressures

Explanation on the Basis of Kinetic Theory. According to the Kinetic theory of gases, the attractive forces between the molecules of the same or different gases are very weak under ordinary conditions of temperature and pressure. Therefore, the molecules of a gaseous mixture move completely independent of one another. As a result, each molecule of the gaseous mixture would strike the unit area of the walls of the container the same number of times per second as if no other molecules were present. Therefore, the pressure due to a particular gas is not changed by the presence of other gases in the container. Consequently, the total pressure exerted by a gaseous mixture must be equal to the sum of the partial pressure of each gas when present alone in that space. Hence the Kinetic theory explains Dalton's Law of Partial Pressures.

Deduction from Kinetic Gas Equation. Let us consider only two gases. According to kinetic gas equation,

$$PV = \frac{1}{3}mnu^2 \quad \text{or} \quad P = \frac{1}{3}\frac{mnu^2}{V}$$

Now, if only the first gas is enclosed in the vessel of volume V, the pressure exerted would be

$$P_1 = \frac{1}{3}\frac{m_1 n_1 u_1^2}{V}$$

Again, if only the second gas is enclosed in the same vessel (so that V is constant), then the pressure exerted would be $P_2 = \frac{1}{3}\frac{m_2 n_2 u_2^2}{V}$

Lastly, if both the gases are enclosed together in the same vessel then since the gases do not react with each other, their molecules behave independent of each other. Hence, the total pressure exerted would be

$$P = \frac{1}{3}\frac{m_1 n_1 u_1^2}{V} + \frac{1}{3}\frac{m_2 n_2 u_2^2}{V}$$
$$= P_1 + P_2$$

Similarly, if more than two gases are present, then it can be proved that $P = P_1 + P_2 + P_3 + \ldots$

2.9. Relation Between Average Kinetic Energy and Absolute Temperature– Deduction from Kinetic Theory

According to Kinetic gas equation,

$$PV = \frac{1}{3}mnu^2 \quad \ldots(i)$$

where P is the pressure, V is the volume of the gas, m is the mass of each molecule, n is the number of molecules present and u is the root mean square speed of the molecules

If 1 mole of the gas is taken, then the total mass of the gas, $m \times n$ = M, the molar mass of the gas. Hence eqn. (*i*) becomes

$$PV = \frac{1}{3}Mu^2 \quad \ldots(ii)$$

It can be re-written as

$$PV = \frac{2}{3} \cdot \frac{1}{2} Mu^2$$

But $\frac{1}{2} Mu^2$ represents the kinetic energy (K.E.) per mole

Hence $\quad PV = \frac{2}{3} \times \text{K.E.}$

or $\text{K.E.} = \frac{3}{2} PV$ for 1 mole of the gas ...(*iii*)

But for 1 mole of the gas, the ideal gas equation is

$$PV = RT$$

Putting this value in eqn. (*iii*), we get

$\text{K.E.} = \frac{3}{2} RT$ for 1 mole of the gas ...(*iv*)

To get average kinetic energy per molecule, divide both sides of eqn. (*iv*) by the Avogadro's number, N *i.e.*, the number of molecules present in one mole of the gas. Thus we have

$$\text{Average K.E.} = \frac{3}{2}\frac{R}{N} T$$

or $\quad \overline{\text{K.E.}} = \frac{3}{2} kT$ ...(*v*)

where $k = \frac{R}{N}$ is called Boltzmann constant

From eqn. (*v*), we observe that

Average K.E. ∝ Absolute temperature of the gas irrespective of the nature of the gas. This is one of the postulates of kinetic theory of gases.

Further, as $\overline{\text{K.E.}} = \frac{1}{2} mu^2$ *i.e.* $\overline{\text{K.E.}} \propto u^2$ and also $\overline{\text{K.E.}} \propto T$, this means that $u^2 \propto T$ or $u \propto \sqrt{T}$. Thus, when T = 0 K, $u = 0$ *i.e.* molecular motion in a gas should become zero at absolute zero. In fact, the gas liquefies before this temperature is attained. The motion of the gas molecules due to temperature is called **thermal motion.**

PROBLEMS ON CALCULATION OF *u*, υ α and KINETIC THEORY

EXAMPLE 1. *At 27°C, a gas contains 10 molecules travelling with a speed of 4 ms⁻¹, 20 molecules travelling with a speed of 5 ms⁻¹ and 40 molecules travelling with a speed of 8 ms⁻¹. Calculate the average speed, root mean square speed and most probable speed of the gas at 27°C.*

Solution. Average speed $(u_{av}) = \frac{\Sigma n_i v_i}{\Sigma n_i}$

$$= \frac{10 \times 4 + 20 \times 5 + 40 \times 8}{10 + 20 + 40} = \frac{460}{70} = \mathbf{6 \cdot 56\ ms^{-1}}$$

Root mean square speed $(u_{r.m.s.})$

$$= \sqrt{\frac{\Sigma n_i v_i^2}{\Sigma n_i}} = \sqrt{\frac{10 \times 4^2 + 20 \times 5^2 + 40 \times 8^2}{10 + 20 + 40}}$$

$$= \sqrt{\frac{160 + 500 + 2560}{70}} = \mathbf{6 \cdot 78\ ms^{-1}}$$

Most probable speed (u_{mp})

$$= 0 \cdot 816 \times u_{r.m.s.}$$

$$= 0 \cdot 816 \times 6 \cdot 78\ ms^{-1} = \mathbf{5 \cdot 53\ ms^{-1}}.$$

EXAMPLE 2 *(a) Calculate the total and average kinetic energy of 32 g methane molecules at 27°C (R = 8·314 JK⁻¹ mol⁻¹)*

(Bihar C.E.E. 1997, N.C.E.R.T.)

(b) Also calculate the root mean square speed of methane molecules at 27°C.

Solution. (*a*) Total K.E. $= \frac{3}{2} nRT$

$$= \frac{3}{2} \times \frac{32}{16}\ \text{mol} \times 8 \cdot 314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}$$

(Molar mass of CH_4 = 16 g mol⁻¹)

$$= \mathbf{7482 \cdot 6\ J}$$

Average K.E.,

$$\overline{\text{K.E.}} = \frac{3}{2} kT = \frac{3}{2} \times \frac{8 \cdot 314\ \text{JK}^{-1}\ \text{mol}^{-1}}{6 \cdot 02 \times 10^{23}\ \text{molecules mol}^{-1}} \times 300\ \text{K}$$

$$= \mathbf{6 \cdot 21 \times 10^{-21}\ J\ molecule^{-1}}$$

or $\quad = \frac{3}{2} RT\ \text{mol}^{-1}$

$$= \frac{3}{2} \times 8 \cdot 314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}$$

$$= \mathbf{3741 \cdot 3\ J\ mol^{-1}}$$

(*b*) $u_{r.m.s.} = \sqrt{\frac{3RT}{M}}$

Using C.G.S. units, put

$R = 8 \cdot 314 \times 10^7\ \text{ergs K}^{-1}\ \text{mol}^{-1}$,

$T = 27 + 273 = 300\ \text{K}$,

M (for CH_4) = 16 g mol⁻¹, we get

$$u_{r.m.s.} = \sqrt{\frac{3 \times 8 \cdot 314 \times 10^7 \times 300}{16}}$$

$$= \mathbf{6 \cdot 839 \times 10^4\ cm\ s^{-1}}$$

$$= \mathbf{683 \cdot 9\ ms^{-1}}$$

Using S.I. units, put R = $8 \cdot 314$ JK^{-1} mol^{-1}, T = 300 K, M = 16×10^{-3} kg mol^{-1}, we get

$$u_{r.m.s.} = \sqrt{\frac{3 \times 8 \cdot 314 \times 300}{16 \times 10^{-3}}}$$

$$= \mathbf{683 \cdot 9\ ms^{-1}}$$

EXAMPLE 3. *The average kinetic energy of a gas molecule at 0°C is $5 \cdot 621 \times 10^{-21}$ J. Calculate Boltzmann constant. Also calculate the number of molecules present in one mole of the gas.*

Solution. Average kinetic energy

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

$$\therefore \quad k = \frac{2}{3} \times \frac{\text{K.E.}}{T}$$

$$= \frac{2}{3} \times \frac{5 \cdot 621 \times 10^{-21}\ \text{J molecule}^{-1}}{273\ \text{K}}$$

$$= \mathbf{1 \cdot 373 \times 10^{-23}\ JK^{-1}\ molecule^{-1}}$$

No. of molecules in 1 mole of the gas

$$(\text{Avogadro's No.}) = \frac{R}{k}$$

$$= \frac{8 \cdot 314\ \text{JK}^{-1}\ \text{mol}^{-1}}{1 \cdot 373 \times 10^{-23}\ \text{JK}^{-1}\ \text{molecule}^{-1}}$$

$$= \mathbf{6 \cdot 055 \times 10^{23}\ molecules\ mol^{-1}}.$$

2.10. Deviations from Ideal Gas Laws— Study of Real Gases

Ideal and Real Gases. *A gas which obeys the ideal gas equation, PV = nRT under all conditions of temperature and pressure is called an 'ideal gas'.* However, there is no gas which obeys the ideal gas equation under all conditions of temperature and pressure. Hence the concept of ideal gas is only theoretical or hypothetical. The gases are found to obey the gas laws fairly well if the pressure is low or the temperature is high. Such gases are therefore known as *'Real gases.'* All gases are real gases. However it is found that gases which are soluble in water or are easily liquefiable e.g. CO_2, SO_2, NH_3 etc. show larger deviations than the gases like H_2, O_2, N_2 etc.

Study of Deviations. The extent to which a real gas deviates from ideal behaviour can be conveniently studied in terms of a quantity 'Z' called the **compressibility factor**, which is defined as

$$\boxed{Z = \frac{PV}{nRT}}$$

(*i*) For an ideal gas, as PV = *n*RT, Z = 1

(*ii*) For a real gas, as PV ≠ *n*RT, Z≠1. Hence two cases arise :

(*a*) When **Z < 1**, (*e.g.* for CH_4, CO_2 etc.) the gas is said to show *negative deviation*. This implies that the gas is *more compressible* than expected from ideal behaviour.

This is also attributed to predominance of attractive forces among the molecules of these gases.

(*b*) When **Z > 1**, the gas is said to show *positive* deviation. This implies that the gas is *less compressible* than expected from ideal behaviour.

This is attributed to the predominance of the strong respulsive forces among the molecules.

Greater the departure in the value of Z from unity, greater are the deviations from ideal behaviour.

At the same temperature and pressure, the extent of deviation depends upon the nature of the gas, as shown in Fig. 2.18 (*a*). Thus at intermediate

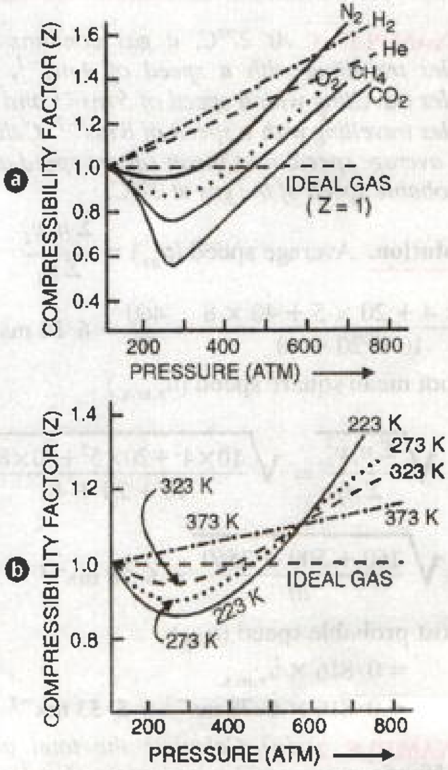


FIGURE 2.18. (a) Z vs P for different gases
(b) Z vs P for N_2 gas at different temperatures.

pressures, CO_2 shows much larger negative deviation than H_2 or N_2.

For the same gas, at a particular pressure, the extent of deviation depends upon temperature, as shown in Fig. 2.18 (*b*) for the case of N_2 gas.

Plots in Fig. (*b*) show that as the temperature increases, the minimum in the curve shifts upwards. Ultimately, a temperature is reached at which the value of Z remains close to 1 over an appreciable range of pressure. For example, in case of N_2, at 323 K, the value of Z remains close to 1 upto nearly 100 atmospheres.*

***The temperature at which a real gas behaves like an ideal gas over an appreciable pressure range is called* Boyle temperature *or* Boyle point.**

Further from the plots shown in Fig. 2.18, it may be seen that at ordinary pressures (1-10 atm), Z is very near to 1 *i.e.* the deviations from ideal behaviour are so small that the ideal gas laws can be applied.

Causes of Deviation from Ideal Behaviour. As explained above, the real gases obey ideal gas equation (PV = *n*RT) only if the pressure is low or the temperature is high. However, if the pressure is high or the temperature is low, the real gases show marked deviations from ideal behaviour. The reasons for such a behaviour shown by the real gases have been found to be as follows :

The derivation of the gas laws (and hence of the ideal gas equation) is based upon the Kinetic Theory of Gases which in turn is based upon certain assumptions. Thus there must be something wrong with certain assumptions. A careful study shows that at high pressure or low temperature, the following two assumptions of Kinetic Theory of Gases are faulty :

(*i*) *The volume occupied by the gas molecules is negligible as compared to the total volume of the gas.*

(*ii*) *The forces of attraction or repulsion between the gas molecules are negligible.*

The above two assumptions are true only if the pressure is low or the temperature is high so that the distance between the molecules is large. However, if the pressure is high or the temperature is low, the gas molecules come close together. Hence under these conditions :

(*i*) The forces of attraction or repulsion between the molecules may not be negligible.

(*ii*) The volume occupied by the gas may be so small that the volume occupied by the molecules may not be negligible.

Equation of State for the Real gases (van der Waal's equation). To explain the behaviour of real gases, J.D. van der Waal, in 1873, modified the ideal gas equation by applying appropriate corrections so as to take into account

(*i*) the volume of the gas molecules, and

(*ii*) the forces of attraction between the gas molecules.

He put forward the modified equation, known after him as **van der Waal's equation.** This equation *for 1 mole of the gas* is

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

and *for n moles of the gas,* it is

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

where '*a*' and '*b*' are constants, called **van der Waal's constants.** Their values depend upon the nature of the gas.

Derivation of van der Waal's equation. Van der Waal's equation has been obtained by modifying the ideal gas equation PV = *n*RT by applying corrections for the volume and pressure.

(*i*) **Correction for volume.** Suppose the volume occupied by the gas molecules is *v*. When the molecules are moving, their effective volume is four times the actual volume *i.e.* 4 *v*. Let us call it *b i.e.* *b* = 4 *v* (called **excluded volume** or **co-volume**). Thus the free volume available to the gas molecules for movement *i.e.*

Corrected volume = (V − *b*) for one mole

or = (V − *nb*) for *n* moles

(*ii*) **Correction for pressure.** A molecule (A) lying within the vessel is attracted equally by other molecules on all sides but a molecule near the wall (B) is attracted (pulled back) by the molecules inside (Fig. 2.19). Hence it exerts less pressure. In other words, observed pressure is less than the ideal pressure. Hence

Corrected pressure = P + *p*

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*It may be pointed out that for H_2 and He, Z > 1 when T ≥ 273 K and increases with increase in pressure. At temperature much below 273 K, Z < 1 even for these gases.

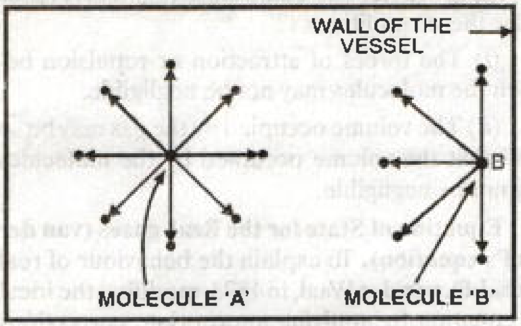


FIGURE 2.19. Backward pull on molecule B by other molecules.

Evidently, the correction term p is proportional to density of the gas near the wall and the density of the gas inside *i.e.*

$$p \propto (\text{density})^2 \text{ or } p \propto d^2$$

But $\quad d \propto \frac{1}{V}$ for one mole

or $\quad d \propto \frac{n}{V}$ for n moles

Hence $p \propto \frac{1}{V^2}$ for one mole or $p = \frac{a}{V^2}$ for one mole

or $\quad p \propto \frac{n^2}{V^2}$ for n moles or $p = \frac{an^2}{V^2}$ for n moles

$\therefore$ Corrected pressure $= \left(P + \frac{a}{V^2}\right)$ for one mole

or $\quad = \left(P + \frac{an^2}{V^2}\right)$ for n moles.

where a is a constant depending upon the nature of the gas.

Substituting the corrected values of volume and pressure in the ideal gas equation, we get

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

or $\quad \left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ for n moles.

Significance of van der Waal's constants

(i) **van der Waal's constant 'a'.** Its value is a measure of the magnitude of the attractive forces among the molecules of the gas. Greater the value of '*a*', larger are the intermolecular forces of attraction.

(ii) **van der Waal's constant 'b'.** Its value is a measure of the effective size of the gas molecules. Its value is equal to four times the actual volume of the gas molecules. It is called *excluded volume* or *co-volume*.

Units of van der Waal's constants

(*i*) Units of 'a'. As

$$p = \frac{an^2}{V^2},$$

$$\therefore \quad a = \frac{p \times V^2}{n^2}$$

$$= \text{atm L}^2 \text{ mol}^{-2} \text{ or bar dm}^6 \text{ mol}^{-2}$$

(*ii*) Units of 'b'. As volume correction

$$v = n\,b,$$

$$\therefore \quad b = \frac{v}{n} = \text{L mol}^{-1} \text{ or dm}^3 \text{ mol}^{-1}$$

Explanation of the behaviour of Real gases by van der Waal's equation

(*i*) At very low pressures, V is very large. Hence the correction term a/V^2 is so small that it can be neglected. Similarly the correction term '*b*' can also be neglected in comparison to V. Thus van der Waal's equation reduces to the form PV = RT. This explains why at very low pressures, the real gases behave like ideal gases.

(*ii*) At moderate pressures, V decreases. Hence a/V^2 increases and cannot be neglected. However V is still large enough in comparison to '*b*' so that '*b*' can be neglected. Thus van der Waal's equation becomes

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

or $\quad PV = RT - \frac{a}{V}$

or $\quad \frac{PV}{RT} = 1 - \frac{a}{RTV}$

or $\quad Z = 1 - \frac{a}{RTV}$

Thus compressibility factor is less than 1. As pressure is increased at constant temperature, V decreases so that the factor a/RTV increases. This explains why initially a dip in the plot of Z versus P is observed.

(*iii*) At high pressures, V is so small that '*b*' cannot be neglected in comparison to V. The factor a/V^2 is no doubt large but as P is very high, a/V^2 can be neglected in comparison to P. Thus van der Waal's equation reduces to the form

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

or $\quad PV = RT + Pb$

or $\quad \frac{PV}{RT} = 1 + \frac{Pb}{RT}$

or $$Z = 1 + \frac{Pb}{RT}$$

Thus compressibility factor is greater than 1. As P is increased (at constant T), the factor Pb/RT increases. This explains why after minima in the curves, the compressibility factor increases continuously with pressure.

(iv) **At high temperatures,** V is very large (at a given pressure) so that both the correction factors (a/V^2 and b) become negligible as in case (*i*). Hence at high temperature, real gases behave like ideal gas.

Explanation of the exceptional behaviour of hydrogen and helium. From Fig. 2.18(*a*), it may be seen that for H_2 and He, the compressibility factor Z is always greater than 1 and increases with increase of pressure. This is because H_2 and He being very small molecules, the intermolecular forces of attraction in them are negligible *i.e.* '*a*' is very very small so that $\frac{a}{V^2}$ is negligible. The van der Waal equation, therefore, becomes

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

or $$PV = RT + Pb$$

or $$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

Thus $\frac{PV}{RT}$ *i.e.* $Z > 1$ and increases with increase in the value of P at constant T.

PROBLEMS ON VAN DER WAAL EQN AND COMPRESSIBILITY FACTOR

EXAMPLE 1. *Calculate the pressure exerted by 110 g of carbon dioxide in a vessel of 2 L capacity at 37°C. Given that the van der Waal's constants are $a = 3{\cdot}59\ L^2\ atm\ mol^{-2}$ and $b = 0{\cdot}0427\ L\ mol^{-1}$. Compare the value with the calculated value if the gas were considered as ideal.*

Solution. According to van der Waal's equation

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

or $$P = \frac{n\,RT}{V - nb} - \frac{an^2}{V^2}$$

Here, $n = \frac{110}{44} = 2{\cdot}5$ moles. Substituting the given values, we get

$$P = \frac{(2{\cdot}5\ \text{mol})\ (0{\cdot}0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (310\ \text{K})}{(2\ \text{L} - 2{\cdot}5\ \text{mol} \times 0{\cdot}0427\ \text{L mol}^{-1})}$$

$$- \frac{(3{\cdot}59\ \text{L}^2\ \text{atm mol}^{-2})\ (2{\cdot}5\ \text{mol}^2)}{(2\ \text{L})^2}$$

$$= 33{\cdot}61\ \text{atm} - 5{\cdot}61\ \text{atm} = \mathbf{28{\cdot}0\ atm}$$

If the gas were considered as ideal gas, applying ideal gas equation

$$PV = n\,RT$$

$$P = \frac{n\,RT}{V}$$

$$= \frac{(2{\cdot}5\ \text{mol})\ (0{\cdot}0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (310\ \text{K})}{2\ \text{L}}$$

$$= \mathbf{31{\cdot}8\ atm}$$

EXAMPLE 2. *Calculate the temperature of 2 moles of sulphur dioxide gas contained in a 5 L vessel at 10 bar pressure. Given that for SO_2 gas, van der Waal's constants are : $a = 6{\cdot}7\ bar\ L^2\ mol^{-2}$ and $b = 0{\cdot}0564\ L\ mol^{-1}$.*

Solution. According to van der Waal's equation

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

$$T = \frac{(P + an^2/V^2)\ (V - nb)}{n\,R}$$

As pressure is in bar, taking R = 0·083 L bar K^{-1} mol^{-1} and substituting the given values, we get

$$T = \frac{[10\ \text{bar} + (6{\cdot}7\ \text{bar L}^2\ \text{mol}^{-2})\ (2\ \text{mol})^2/(5\ \text{L})^2]\ (5\ \text{L} - 2\ \text{mol} \times 0{\cdot}0564\ \text{L mol}^{-1})}{2\ \text{mol} \times 0{\cdot}083\ \text{L bar K}^{-1}\ \text{mol}^{-1}}$$

$$= \frac{(10\ \text{bar} + 1{\cdot}072\ \text{bar})\ (5\ \text{L} - 0{\cdot}1128\ \text{L})}{2 \times 0{\cdot}083\ \text{L bar K}^{-1}}$$

$$= \mathbf{326\ K}$$

EXAMPLE 3. *One mole of SO_2 gas occupies a volume of 350 mL at 27°C and 50 atm pressure. Calculate the compressibility factor of the gas. Comment on the type of deviation shown by the gas from ideal behaviour.*

Solution. Compressibility factor, $Z = \frac{PV}{n\,RT}$

Substituting, $n = 1$ mol, P = 50 atm, V = 350 × 10^{-3} L = 0·35 L

$R = 0\cdot0821$ L atm K^{-1} mol^{-1}, $T = 27 + 273 = 300$ K, we get

$$Z = \frac{(50 \text{ atm})(0\cdot35 \text{ L})}{(1 \text{ mol})(0\cdot0821 \text{ L atm K}^{-1} \text{ mol}^{-1})(300 \text{ K})}$$
$$= 0\cdot711$$

For ideal gas, $Z = 1$. As for the given gas $Z < 1$, it shows *negative* deviation *i.e.* it is *more compressible* than expected from ideal behaviour.

- EXAMPLE. *The van der Waal's constant 'b' for oxygen is* $0\cdot0318$ *L* mol^{-1}. *Calculate the diameter of the oxygen molecule.*

Solution. $b = 4v$

$$\text{or } v = \frac{b}{4} = \frac{0\cdot0318}{4} = 7\cdot95 \times 10^{-3} \text{ L mol}^{-1}$$
$$= 7\cdot95 \text{ cm}^3 \text{ mol}^{-1}$$

$\therefore$ Volume occupied by one O_2 molecule

$$= \frac{7\cdot95}{6\cdot02 \times 10^{23}}$$
$$= 1\cdot32 \times 10^{-23} \text{ cm}^3$$

Considering the molecule to be spherical,

$$\frac{4}{3}\pi r^3 = 1\cdot32 \times 10^{-23}$$
$$\text{or} \quad r^3 = \frac{3}{4} \times \frac{7}{22} \times 1\cdot32 \times 10^{-23}$$
$$= 3\cdot15 \times 10^{-24}$$
$$\therefore \quad 3 \log r = \log(3\cdot15 \times 10^{-24})$$
$$= -24 + 0\cdot4983$$
$$= -23\cdot5017$$
$$\text{or} \quad \log r = -7\cdot8339 = \bar{8}\cdot1661$$
$$\therefore \quad r = \text{Antilog } \bar{8}\cdot1661$$
$$= 1\cdot466 \times 10^{-8} \text{ cm}$$

$\therefore$ Diameter of oxygen molecule

$$= 2 \times r = 2\cdot932 \times 10^{-8} \text{ cm}$$
$$= 2\cdot932 \text{ Å}$$

PROBLEMS FOR PRACTICE

1. Calculate the pressure exerted by $10\cdot2\,g$ of NH_3 in a $3\cdot0$ dm^3 vessel at 25°C (*a*) using ideal gas equation (*b*) using van der Waal's equation. The van der Waal's constants are : $a = 4\cdot17$ dm^6 atm mol^{-2}, $b = 0\cdot0371$ dm^3 mol^{-1} [Ans. (*a*) 4·9 atm (*b*) 4·8 atm]

2. 180 *g* of steam is contained in a vessel of 25 L capacity under a pressure of 50 atm. Calculate the temperature of the steam. Given that for water vapour. $a = 5\cdot46$ bar L^2 mol^{-2} and $b = 0\cdot031$ L mol^{-1}. [Ans. 1531·7 K]

Difference between Ideal gas and Real gas. The main points of difference are summed up in the table below :

Ideal gas	Real gas
(*i*) It obeys gas laws under all conditions of temperature and pressure.	(*i*) It obeys gas laws only under low pressure and high temperature.
(*ii*) No gas is ideal.	(*ii*) All gases are real.
(*iii*) Volume occupied by the molecules is negligible as compared to the total volume occupied by the gas.	(*iii*) Volume occupied by the molecules is not negligible as compared to the total volume occupied by the gas.
(*iv*) The forces of attraction among the molecules of the gas are negligible.	(*iv*) The forces of attraction among the molecules cannot be neglected at high pressure and low temperature.
(*v*) It obeys the ideal gas equation $PV = nRT$	(*v*) It obeys van der Waal's equation $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

2.11. Liquefaction of Gases and Critical Temperature

The liquefaction of a gas takes place when the intermolecular forces of attraction become so high that they bind the gas molecules together to form the liquid state. The intermolecular forces of attraction can be increased either by increasing the pressure so that the molecules come close together or by cooling the gas so that the kinetic energy of the molecules decreases and they become slower. Hence *a gas can be liquefied by cooling or by application of pressure or the combined effect of both.*

Gases like ammonia, sulphur dioxide, hydrogen chloride, carbon dioxide etc. could be liquefied by any one of the modes mentioned above *i.e.* either by application of pressure (at room temperature) or by cooling (at atmospheric pressure). However, the effect of temperature on the liquefaction of gases is found to be very important as higher the temperature of the gas, more difficult it is to liquefy it and higher is the pressure required. For example, pressures required to liquefy carbon dioxide at different temperatures are given below :

Temp. (°C)	—50	—30	—10	10	20	30	31·1
Pressure (atm)	6·7	14·1	26·1	44·4	56·5	71·2	73·9

Further, it is observed that gases like hydrogen, helium, oxygen nitrogen etc. could not be liquefied at room temperature by application of pressure alone, howsoever high it may be. Hence at one time, these gases were called 'permanent gases'. Now it is well known that each of these gases could also be liquefied provided first it is cooled down to or below a particular temperature. In other words, for each gas, there is a particular temperature above which it cannot be liquefied, howsoever high pressure may be applied on the gas. This temperature is known as critical temperature. Thus

Critical temperature of a gas may be defined as that temperature above which it cannot be liquefied howsoever high pressure may be applied on the gas.

The pressure required to liquefy the gas at the critical temperature is called **critical pressure.** The volume occupied by one mole of the gas at the critical temperature and the critical pressure is called the **critical volume.** All the three collectively are called critical constants of the gas and are represented by T_c, P_c and V_c. For example, critical constants of CO_2 are :

$$T_c = 31 \cdot 1°C,$$

$$P_c = 73 \cdot 9 \text{ atm},$$

$$V_c = 95 \cdot 6 \text{ cm}^3 \text{ mol}^{-1}$$

Critical constants of a few gases are given in Table 2.2 below :

TABLE 2.2. Critical constants of some gases.

Gas	T_c (K)	P_c (atm)	V_c (cm^3 mol^{-1})
He	5·3	2·29	57·7
H_2	33·2	12·97	65·0
N_2	126·0	33·9	90·0
CO	134·0	35·0	93·0
O_2	154·3	50·4	74·4
CH_4	190·6	45·6	98·7
CO_2	304·15	73·9	95·6
NH_3	405·5	113·0	72·3

It is interesting to mention here that Andrews in 1861 was the first to study the critical phenomena experimentally using CO_2 gas. He studied the effect of pressure on the volume of CO_2 at different constant temperatures. Some of the isotherms thus obtained are shown in Fig. 2.20.

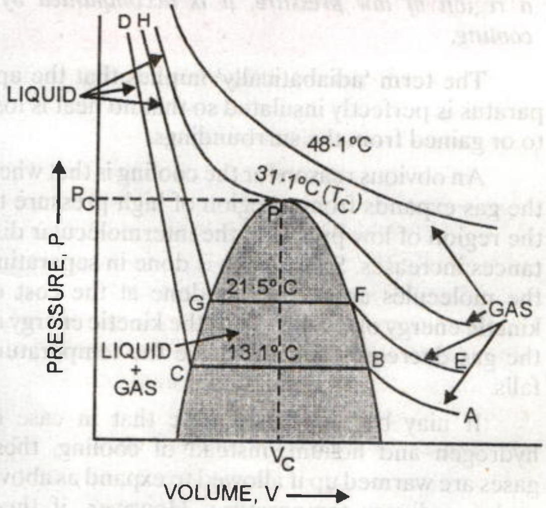


FIGURE 2.20. Isotherms of CO_2 (From Andrew's experiment)

At the lowest temperature employed *i.e.* 13·1°C, at low pressure CO_2 exists as a gas, as shown at the point A. As the pressure is increased, the volume of the gas decreases along the curve AB. At B liquefaction of the gas starts. Hence volume decreases rapidly along BC because liquid has much less volume than the gas. At the point C, liquefaction is complete. Now the increase in pressure has very little effect upon volume because liquids are very little compressible. Hence a steep curve CD is obtained. As the temperature is increased, horizontal portion becomes smaller and smaller and at 31·1°C, it is reduced at a point, P. This means that above 31·1°C, the gas cannot be liquefied at all, however high pressure may be applied. Thus 31·1°C is the critical temperature. The corresponding pressure to liquefy the gas at the critical temperature is its critical pressure, P_c (*i.e.* 73·9 atm). The volume occupied by 1 mole of the gas under these conditions is its critical volume, V_c (*i.e.* 95·6 ml).

2.12. Methods for Liquefaction of Gases

Two methods most commonly used for liquefaction of gases are briefly described below :

1. By the adiabatic expansion of compressed gas-Linde's Process. This process is based upon **Joule-Thomson effect** which states as follows :

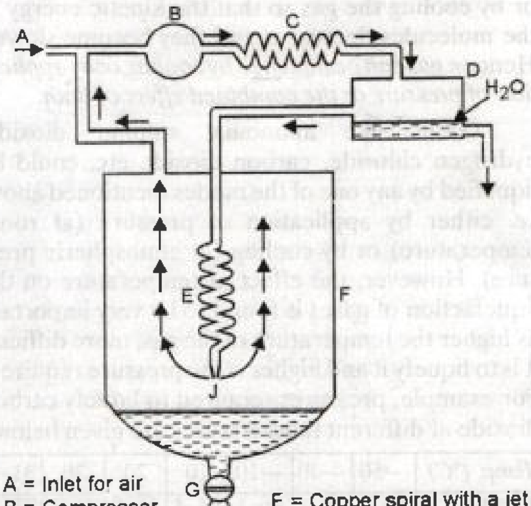
When a gas under high pressure is allowed to expand adiabatically through a fine orifice (hole) into a region of low pressure, it is accompanied by cooling.

The term 'adiabatically' implies that the apparatus is perfectly insulated so that no heat is lost to or gained from the surroundings.

An obvious reason for the cooling is that when the gas expands from a region of high pressure to the region of low pressure, the intermolecular distances increases. Some work is done in separating the molecules apart. This is done at the cost of kinetic energy of the gas. Thus the kinetic energy of the gas decreases and therefore the temperature falls.

It may be mentioned here that in case of hydrogen and helium, instead of cooling, these gases are warmed up if allowed to expand as above, under ordinary temperature. However, if these gases are first cooled to some particular temperature and then allowed to expand, they behave like other gases. The temperature to which a gas should thus be cooled is called the *inversion temperature.* The inversion temperatures for hydrogen and helium are −80°C and −240°C respectively.

The process based upon the above principle is known as **Linde's process.** The apparatus used is in shown in Fig. 2.21. The chart showing the names of the different parts is also given in the Fig. 2.21.



A = Inlet for air
B = Compressor
C = Condensing coils
D = Receiver for water
E = Copper spiral with a jet J
F = Outer chamber
G = Outlet for liquefied air

FIGURE 2.21. Linde's process for liquefaction of air.

The above apparatus was used by Linde for the liquefaction of air. The procedure adopted is as follows :

The air is first compressed to about 200 atmosphere in the compressor B and then passed through the condensing coils C. As a result, the air is cooled and the water vapour present condense to form the liquid which is removed. The dry air is then passed through the copper spiral E which terminates into a jet J. The air expands through the jet J into the chamber F where the pressure of the air falls down to about 50 atmospheres. Thus as a result of Joule-Thomson effect, the air is cooled. As the cooled air moves up, it further cools the incoming air. The cooled air is sent to the compressor again and the process is repeated a number of times till ultimately the air is cooled to such an extent that it liquefies. The liquefied air collects at the bottom of the chamber F and can be drawn off. Any uncondensed air is recirculated.

2. By the adiabatic expansion of compressed gas involving mechanical work-Claude's process. This process is based upon the principle that when a gas expands adiabatically against a piston in an engine, it does some external work ; hence its internal energy falls and consequently the temperature of the gas falls. This principle, combined with the Joule-Thomson effect, has been applied in the Claude's process for the liquefaction of air. The apparatus used in shown in Fig. 2.22.

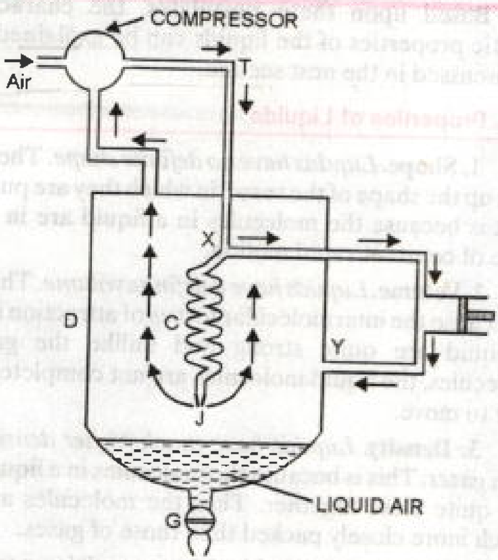


FIGURE 2.22. Claude's process.

The purified air *i.e.* air freed from carbon dioxide and water vapour is first compressed to about 200 atmospheres. The compressed air then passes through the tube T which bifurcates at the point X. A part of the air goes into the cylinder fitted with an air tight piston and the rest of the air passes through the coil C having a jet J at its end. The air that goes into the cylinder pushes the piston and thus does some external work. As a result, the internal energy of the air falls and hence the temperature falls. The cooled air then enters the chamber D at the point Y. The air that passes through the coil C is cooled by Joule-Thomson effect as it comes out of the jet J into the chamber D. The cooled air going upwards in the chamber D further cools the incoming air in the coil C. The cooled air is led to the compressor and the process is repeated a number of times till the air is cooled to such an extent that it liquefied. The liquefied air collects in the chamber and is withdrawn.

2.13. Importance of Critical Temperature

The critical temperature of a gas is a measure of the strength of the intermolecular forces of attraction of that gas. Weaker are the intermolecular forces, more difficult it is to liquefy that gas and hence lower would be the critical temperature of that gas. For example, helium and hydrogen have weak intermolecular forces. Thus they are difficult to liquefy and have low critical temperatures. On the other hand, CO_2 and NH_3 have strong intermolecular forces of attraction, they can be easily liquefied and their critical temperatures are high which are above room temperature. Further, as already discussed, van der Waal's constant '*a*' is also a measure of the intermolecular forces of attraction. Hence it is found that the values of the constant '*a*' increase in the same order as the critical temperature. A comparision of van der Waal's constant '*a*' and the critical temperature, T_c, for a few gases is given below :

Gas	He	H_2	N_2	CO	CO_2	NH_3
T_c (*K*)	5·2	33·2	126·2	134·0	304·2	405·0
a ($atm L^2 mol^{-2}$)	0·0341	0·244	1·39	1·49	3·59	4·17

ADD TO YOUR KNOWLEDGE

1. Like van der Waal's equation, many other equations of state have been put forward. The most satisfactory and general expression is Kammerlingh—Onnes equation viz. $PV = A + BP + CP^2 + DP^3 + ...$ where A, B, C etc. are called first, second, third etc. **virial coefficients.** At very low pressure, first virial coefficient, *i.e.* A = RT.
2. Van der Waal's constant '*a*' is related to the ease of liquefaction of the gas. Greater the value of '*a*', greater are the intermolecular forces of attraction and hence more easily the gas is liquefied *e.g.* for a few gases, its value is in the order $SO_2 > Cl_2 > NH_3 > HCl$.

ADD TO YOUR KNOWLEDGE CONTD.

3. At the critical point, the densities of the substance in the gaseous state and liquid state are same and there is no distinction between the two states.

4. Fluids above the critical temperature are called *super critical fluids.* They dissolve many organic substances. They are used for quick separation of a mixture into its components.

5. CO_2 above 31·1°C and above 600 bar pressure has a density of about 1 g/cm^3. It is used to dissolve out caffeine from coffee beans as it is a better substitute than chlorofluorocarbons which are harmful for the environment.

SECTION—II
THE LIQUID STATE

2.14. Introduction

The liquids differ from gases in one important aspect *i.e.* whereas in case of gases the molecules are far apart from each other so that the volume occupied by the molecules as well as the forces of attraction between them are considered to be negligible, this is not so in case of liquids. In a liquid, the molecules are quite close together so that there are considerable forces of attraction between them and hence they are held together into a definite volume. However, these forces of attraction are not as large as exist between the constituent atoms, ions or molecules of a solid which fix these particles into definite positions so that the solids have a definite volume as well as a definite shape and a perfectly ordered arrangement of their constituent particles. The liquids possess fluidity like gases but incompressibility like solids. As a matter of fact, *a liquid state may be considered as an intermediate state between the gas and the solid.*

The behaviour of liquids as explained above gives some characteristic properties to the liquids such as *a definite volume but no definite shape, incompressibility, diffusion, fluidity* (or viscosity), *evaporation* (or vapour pressure), *surface tension* etc. These properties can be explained on the basis of **'Kinetic molecular theory of liquids'** which is based upon the following postulates :

(*i*) *A liquid is made up of molecules.*

(*ii*) *The molecules of the liquid are quite close together.*

(*iii*) *The intermolecular forces of attraction in a liquid are quite large.*

(*iv*) *The molecules of a liquid are in a state of constant rapid motion.*

(*v*) *The average kinetic energy of the molecules of a liquid is directly proportional to their absolute temperature.*

Based upon these postulates, the characteristic properties of the liquids can be explained, as discussed in the next section.

2.15. Properties of Liquids

1. Shape. *Liquids have no definite shape.* They take up the shape of the vessel in which they are put. This is because the molecules in a liquid are in a state of constant rapid motion.

2. Volume. *Liquids have a definite volume.* This is because the intermolecular forces of attraction in a liquid are quite strong and unlike the gas molecules, the liquid molecules are not completely free to move.

3. Density. *Liquids have much higher density than gases.* This is because the molecules in a liquid are quite close together. Thus the molecules are much more closely packed than those of gases.

4. Compressibility. *Liquids are much less compressible than gases.* This is because the intermolecular distances of separation are much smaller in liquids than in gases.

5. Diffusion. *Liquids diffuse like gases but the diffusion is much slower.* This is because the liquid molecules are quite close, they undergo a much larger number of collisions with each other.

6. Vapour Pressure. Suppose some liquid is placed in an evacuated vessel connected to a manometer as shown in Fig. 2.23. According to

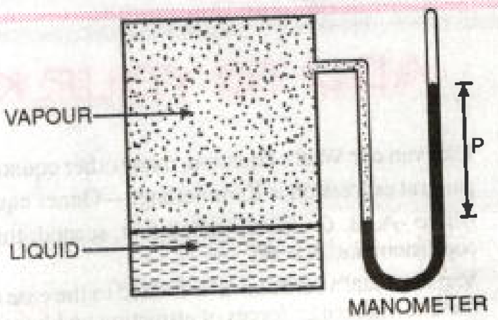


FIGURE 2.23. Concept of vapour pressure of a liquid.

kinetic theory of liquids, the molecules of the liquid are constantly moving in different directions with different speeds. Thus as these molecules are moving with different speeds, they possess different kinetic energies. At any particular temperature, the energy of some of the molecules may be so high that they may overcome the forces of attraction by the neighbouring molecules and may leave the liquid and come in the space above the liquid. This process is called *evaporation*. As the time passes, more and more molecules of the liquid leave the liquid and come in the space above the liquid. The molecules thus present above the liquid are called *vapour*. The molecules in the vapour phase are also constantly moving and some of them strike the surface of the liquid and may be recaptured by the liquid. The process is called *condensation*.

If the liquid is added into the evacuated vessel, then initially, as there are no molecules of the vapour, the rate of condensation is zero. However, *if the temperature is kept constant, the evaporation continues at constant rate**, as shown in Fig. 2.24, by the straight line plot. However, with the passage of time, as the number of molecules in the vapour phase becomes more and more, the rate of condensation also increases (Fig. 2.24). Ultimately, a stage is reached when rate of condensation becomes equal to the rate of evaporation *i.e.* as many molecules re-enter into the liquid as leave the liquid in the same time. This state is called the state of equilibrium. The pressure exerted by the vapour at this stage (as indicated on the manomerter) is called vapour pressure or sometimes called saturated vapour pressure as the vapour phase is saturated with vapour at this stage.

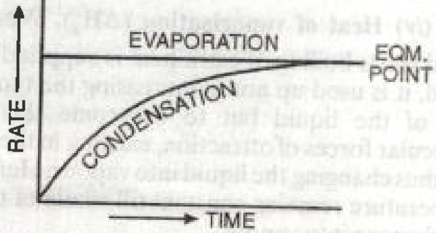


FIGURE 2.24. Time dependence of rate of evaporation and rate of condensation in a closed vessel and attainment of equilibrium.

Hence

Vapour pressure of a liquid at any temperature may be defined as the pressure exerted by the vapour present above the liquid in equilibrium with the liquid at that temperature.

Some Important Results. Some important results related with the process of evaporation are given below :

(*i*) **Cooling caused by evaporation.** When a liquid evaporates, the more energetic molecules leave the liquid. As a result, the average kinetic energy of the remaining liquid decreases and hence the temperature falls.

(*ii*) **Factors affecting vapour pressure.** Two important factors on which the vapour pressure of a liquid depends are :

(*a*) **Nature of the liquid.** If the intermolecular forces of attraction in the liquid are weak, the molecules can easily leave the liquid and come into the vapour phase and hence the vapour pressure is higher. For example, the vapour pressure of acetone, benzene etc. is higher than that of water at the same temperature (as shown in Fig. 2.25).

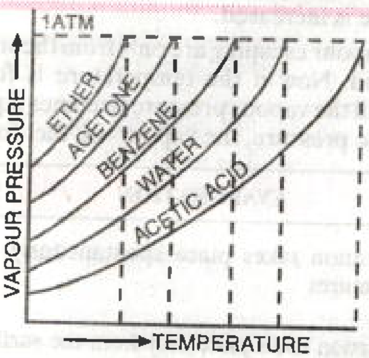


FIGURE 2.25. Vapour pressure-Temperature curves for some liquids.

(*b*) **Effect of temperature.** As the temperature of a liquid is increased, the vapour pressure of the liquid increases. This is evident from each curve in Fig. 2.25.

The increase of vapour pressure with increase in temperature can be explained on the basis of Maxwell's distribution of energies. At a particular temperature, all the molecules do not have the same energy. A plot of the fractions of molecules versus their corresponding kinetic energies is as

---

*This is because according to Maxwell-Boltzmann law, the fraction of molecules having energy more than a particular value, E at temperature T is given by Boltzmann factor, $e^{-E/RT}$

shown in Fig. 2.26. Only those molecules can escape from liquid into the vapour phase whose kinetic energy is more than E as shown in the Fig. 2.26. With increase in temperature, the curve shifts as shown. The fraction of molecules with kinetic energy greater than E increases. As a result, the molecules escaping into the vapour phase increases and so does the vapour pressure.

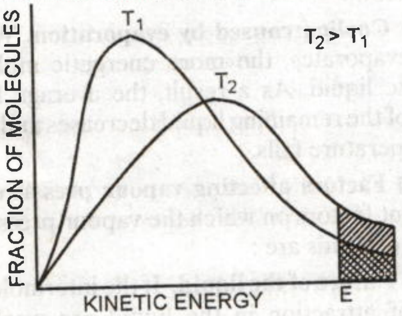


FIGURE 2.26. Maxwell's energy distribution curves at temperatures T_1 and T_2 ($T_2 > T_1$)

***(iii)* Boiling Point.** As stated above, the vapour pressure of a liquid increases as the temperature is increased.

The vapour escaping are only from the surface of the liquid. Now if the temperature is further increased till the vapour pressure becomes equal to atmospheric pressure, the vapour in the form of bubbles from below the surface start rising to the surface and escape into the air. The temperature at which this happens is called the boiling point. Thus

Boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the external pressure (i.e. the atmospheric pressure).

When the external pressure is normal atmospheric pressure (*i.e.* 760 mm), the boiling point is called the *normal boiling point.* For example, normal boiling point of water is 100°C. The normal boiling point for any liquid is obtained from the vapour pressure-temperature curves, as shown in Fig. 2.25.

Obviously if the external pressure is higher, more heat will be required to make the vapour pressure equal to the external pressure and hence higher will be the boiling point. Similarly, if the external pressure is decreased, the boiling point is lowered. This is the reason that a liquid boils at a lower temperature on the top of a mountain (where pressure is low) than on the sea shore. Further this principle is used for purifying the unstable liquids by distillation under reduced pressure.

Difference between Boiling and Evaporation. Although boiling and evaporation are similar processes, yet they differ in the following two respects :

EVAPORATION	BOILING
1. Evaporation takes place spontaneously at all temperatures	1. Boiling takes place at a particular temperature where vapour pressure becomes equal to atmospheric pressure.
2. Evaporation takes place only from the surface of the liquid	2. Boiling involves the formation of bubbles of the vapour below the surface of the liquid (Fig. 2.27).

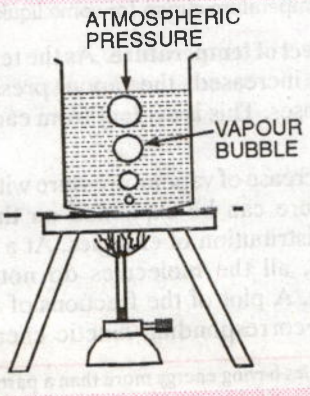


FIGURE 2.27. Boiling of a liquid.

***(iv)* Heat of vaporisation** (ΔH_v). When the liquid starts boiling, if extra heat is supplied to the liquid, it is used up not in increasing the temperature of the liquid but to overcome the intermolecular forces of attraction, existing in the liquid and thus changing the liquid into vapour. Hence the temperature remains constant till whole of the liquid changes into vapour.

The amount of heat required to change 1 mole of the liquid into its vapour at the boiling point is called the heat of vaporisation of the liquid.

Obviously, greater the intermolecular forces of attraction present in a liquid, greater is the heat of vaporisation and higher is the boiling point. For example, the heat of vaporisation and boiling point of water are more than those of ether, acetone, benzene etc.

7. Surface tension. Surface tension is a characteristic property of liquids which arises due to the fact that the molecules of the liquid at the surface are in different situation than those in the interior of the liquid. For example, a molecule lying inside the liquid is surrounded by other molecules and so is attracted equally in all directions (Fig. 2.28). Hence the net force of attraction acting on the molecule is zero. However, a molecule lying at the surface is attracted more by the molecules lying in the bulk of the liquid than by the molecules lying above it in the vapour phase. Thus a molecule lying at the surface experiences a net inward attraction. As a result of this inward pull on all molecules lying at the surface, the surface behaves as if it were under tension (like a stretched membrane). Due to this property of liquids, surface experiences a net inward attraction. That is why this property of liquids is called surface tension. Hence

Surface tension of a liquid is defined as the force acting at right angles to the surface along one centimetre length of the surface. Thus the units of surface tension are dynes per cm (or Newtons per metre i.e. Nm^{-1} ***in the S.I. system).***

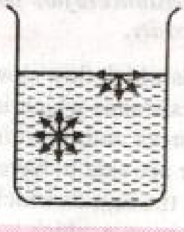


FIGURE 2.28. Surface tension of a liquid.

Further, as a result of the inward pull on the molecules at the surface, the surface of the liquid tends to contract to the smallest possible area for a given volume of the liquid. It is for this reason that the drops of a liquid are spherical because for a given volume, a sphere has minimum surface area.

To increase the area of the surface, some work has to be done against the inward pull. For example, consider a soap-solution film contained in rectangular wire frame ABCD in which the side CD is movable (Fig. 2.29). In order to extend the surface area of the film, the movable wire has to be pulled from position CD to position EF. Thus some work has to be done against the force of surface tension.

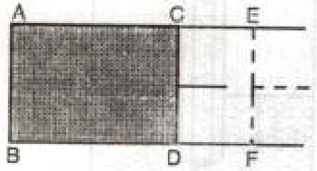


FIGURE 2.29. Concept of surface energy.

The work in ergs required to be done to increase or extend the surface area by 1 sq. cm is called surface energy. The units of surface energy are, therefore, ergs per sq. cm (or joules per sq. metre i.e. Jm^{-2} ***in S.I. system).***

In terms of dimensions,

$$
\begin{aligned}
\text{Surface energy} &= \text{work per sq. cm.}\\
&= (\text{Force} \times \text{length}) \text{ per sq. cm.}\\
&= \frac{\text{dynes} \times \text{cm}}{\text{cm}^2} = \text{dynes cm}^{-1}.
\end{aligned}
$$

These units are the same as those of surface tension. Thus the surface energy is same thing as surface tension. Hence the definition of surface energy is sometimes taken as the definition of surface tension.

Some Important Results. Some important results related with the property of surface tension are briefly described below :

(i) Spherical shape of drops. As already explained, surface tension tries to decrease the surface area of the liquid to the minimum. The drops of a liquid (or the bubbles of a gas) are spherical because for a given volume, a sphere has minimum surface area (Fig. 2.30).

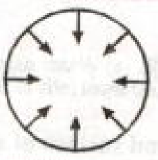


FIGURE 2.30. Inward pull of surface tension makes a drop spherical.

(ii) Rise of a liquid in a capillary tube. Suppose one end of a capillary tube is put into a liquid that wets glass (Fig. 2.31). It is found that the liquid rises into the capillary tube to a certain height. This rise is obviously due to the inward pull of surface

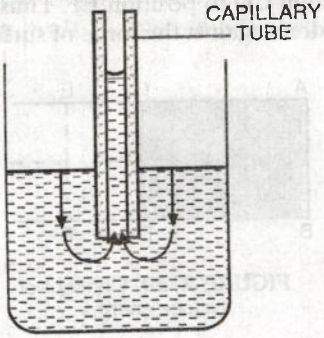


FIGURE 2.31. Rise of a liquid in a capillary tube.

tension acting on the surface which pushes the liquid into the capillary tube. It is because of the same reason that oil rises into the wick of an oil lamp or water below the surface of the earth rises in the plants through the roots or ink rises in a blotting paper.

It may be mentioned here that in case of liquids which do not wet glass *e.g.* mercury, the level inside the capillary falls below the level outside (Fig. 2.32). Further, whereas the upper surface of a liquid that wets glass is concave, that of mercury is convex.

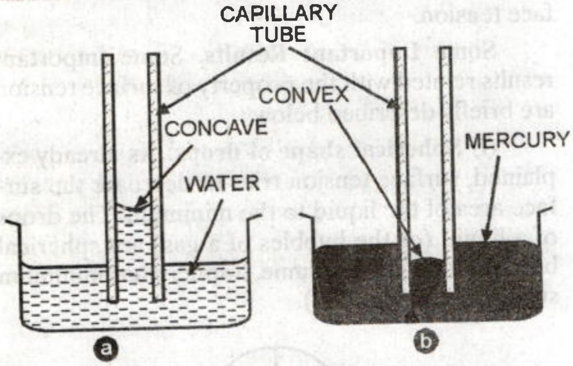


FIGURE 2.32. (a) Water rises in the capillary (b) Mercury level falls in the capillary.

Such a curved surface of a liquid is known as **meniscus.** The concave meniscus of water and the convex meniscus of mercury in a glass tube may be explained on the basis of **'cohesive'** and **'adhesive'** forces. The attractive forces existing between the molecules of the same substance are known as **cohesive forces** *e.g.* between the molecules of water or molecules of mercury etc. whereas those existing between the molecules of different substances are known as **adhesive forces** *e.g.* between water and glass or mercury and glass etc. In case of water taken in a glass tube, adhesive forces are stronger than cohesive forces whereas it is reverse for mercury taken in a glass tube.

(iii) Effect of temperature on surface tension. The surface tension of liquids generally decreases with increase of temperature and becomes zero at the critical temperature (where the meniscus between the liquid and the vapour disappears). The decrease in surface tension with increase of temperature is obviously due to the fact that with increase of temperature the kinetic energy of the molecules (and hence the speeds of molecules) increases and, therefore, the intermolecular attraction decreases.

8. Viscosity. It is well known that all liquids do not flow with the same speed. Some liquids like water, ether etc, flow rapidly while some other liquids like glycerine, castor oil etc. flow quite slowly. This indicates that every liquid has some internal resistance to flow.

This internal resistance to flow possessed by a liquid is called its viscosity.

The liquids which flow slowly, obviously have high internal resistance which is due to strong intermolecular forces and, therefore, are said to be more viscous or are said to have high viscosity. On the other hand, the liquids which flow rapidly have low internal resistance which is due to weak intermolecular forces and hence are said to be less viscous or are said to have low viscosity.

To understand the nature of the internal resistance or friction existing within a liquid, consider a liquid flowing through a narrow tube (Fig. 2.33).

FIGURE 2.33. Flow through a narrow tube.

All parts of the liquid do not move through the tube with the same velocity. Imagine the liquid to be made up of a large number of thin cylindrical coaxial layers. The layer which is in contact with the walls of the tube is almost stationary.

As we move from the walls towards the centre of the tube, the velocity of the cylindrical layers keeps on increasing till it is maximum at the centre. Conversely, we may say that as we move from the centre towards the walls, the velocity of the layers keeps on decreasing. In other words, every layer offers some resistance or friction to the layer immediately below it.

This force of friction which one part of the liquid offers to another part of the liquid is called viscosity.

The flow of a liquid on a fixed horziontal surface may be represented in a similar manner as follows :

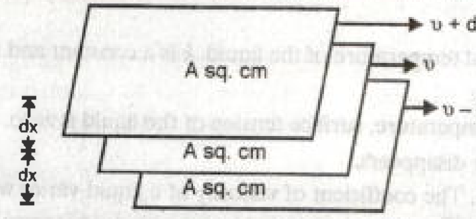


FIGURE 2.34. Representing flow of three layers above the fixed horizontal surface.

It has been found that the force of friction (f) between two layers each having area 'A' sq. cm, separated by a distance dx cm, and having a velocity difference of dv cm/sec, is given by

$$f \propto A\frac{dv}{dx} \quad \text{or} \quad f = \eta\, A\frac{dv}{dx}$$

where η is a constant known as coefficient of viscosity. dv/dx is called **velocity gradient.**

If $dx = 1$ cm, A = 1 sq. cm and $dv = 1$ cm/sec, then $f = \eta$. Hence

Coefficient of viscosity may be defined as the force of friction (in dynes) required to maintain a velocity difference of 1 cm/sec between two parallel layers, 1 cm apart and each having an area of 1 sq.cm

Some Important Results. Some important results related with the property of viscosity are as follows :

(i) Units of viscosity. As already described,

$$f = \eta\, A\frac{dv}{dx}$$

$$\therefore \quad \eta = \frac{f.dx}{A.dv} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm/sec}}$$

$$= \text{dynes cm}^{-2}\ \text{sec.}$$

Thus the units of viscosity are dynes sec cm^{-2}. This quantity is called **1 poise (derived from the name of the pioneer worker, Poiseuille, in the** field of viscosity).

As force = mass × acceleration

i.e. $f = m \times a$, we can also write

$$\eta = \frac{m \times a \times dx}{A\,.\,dv} = \frac{g \times cm\, s^{-2} \times cm}{cm^2 \times cm\, s^{-1}}$$

$$= g\ cm^{-1}\, s^{-1}$$

i.e. 1 poise = 1 $g\ cm^{-1}\, s^{-1}$

Sometimes smaller units like centipoise and millipoise are also used (1 centipoise = 10^{-2} poise, 1 millipoise = 10^{-3} poise)

$$\textbf{In SI units, } \eta = \frac{f\,dx}{A\,dv} = \frac{N \times m}{m^2 \times ms^{-1}}$$

$$= Nm^{-2}s \text{ or Pa s}$$

or in place of $g\ cm^{-1}\, s^{-1}$, we have $kg\, m^{-1}\, s^{-1}$

$$1 \text{ poise} = \frac{1}{10}\text{th of SI unit.}$$

(ii) Effect of temperature on viscosity. With increase of temperature, the kinetic energy of the molecules of the liquid increases. Hence the liquid starts flowing faster. In other words, the viscosity of a liquid decreases with increase in temperature. It has been found that the decrease is about 2% per degree rise of temperature.

ADD TO YOUR KNOWLEDGE

1. **Surfactants.** Soaps and detergents which when added to water decrease its **surface tension** are called **'surfactants'** (surface active agents).
2. **Trouton's Rule.** For liquids which are non-associated and which do not have too high boiling points, the ratio of the heat of vaporisation to the boiling point is approximately 88 JK^{-1} *i.e.* $\frac{\Delta H_v}{T_b} \simeq 88\ \text{JK}^{-1}$.
3. **Guldberg's Rule.** The boiling point of a liquid is nearly two-third of its critical temperature when both are expressed on absolute scale *i.e.* $T_b = \frac{2}{3} T_c$
4. The reciprocal of the coefficient of viscosity of a liquid is called its fluidity *i.e.* $\phi = \frac{1}{\eta}$
5. **Effect of temperature on surface tension (Eotvos equation).** Quantitatively, the effect of temperature on surface tension (γ) is given by Eotvos equation, viz.

$$\gamma = k\,(t_c - t)\left(\frac{\rho}{M}\right)^{2/3}$$

where ρ is density, M is molecular mass and t_c is the critical temperature of the liquid. k is a constant and t is the temperature at which measurement is made.

Thus, when $t = t_c$, $\gamma = 0$. This means that at the critical temperature, surface tension of the liquid is zero. At this point, the meniscus between the liquid and the vapour disappears.

6. **Effect of temperature on viscosity (Arrhenius equation).** The coefficient of viscosity of a liquid varies with temperature according to the equation $\eta = A\,e^{E_a/RT}$

where A and E_a are constants for the given liquid and E_a is called activation energy for viscous flow.

SECTION—III

THE SOLID STATE

2.16. Introduction

We have already discussed that in a solid, the constituent particles (atoms, ions or molecules) are most closely packed and have the strongest intermolecular forces of attraction. As a result, the particles are fixed in their position and do not have any freedom of motion except that of vibration about their mean position. This gives rise to the following characteristic properties to a solid :

(*i*) Rigidity

(*ii*) A definite shape and a definite volume

(*iii*) Incompressibility

(*iv*) Poor diffusability through them

(*v*) No fluidity

Thus a solid may be defined as that form of matter which possesses rigidity and hence a definite shape and a definite volume.

2.17. Classification of Solids

The various solids are classified into the following two types :

(1) Crystalline solids. All solid elements and compounds exist in this form.

(2) Amorphous solids *e.g.* rubber, glass, pitch, fused silica, polymers of high molecular mass etc.

Points of Difference between a Crystalline solid and an Amorphous solid.

(*i*) **Arrangement of their constituent particles.** In a crystalline solid, the constituent particles (*i.e.* ions, atoms or molecules) are arranged in a definite geometric pattern in all the three dimensions. In fact, the order is so regular that knowing the arrangement at any one site, that at any other site can be predicted. This is called *long range order*. On the other hand, in an amorphous solid, there is a regular arrangement of particles in a small region only. This is called *short range order*. Thus whereas crystalline solids possess both short range and long range order, amorphous solids possess only short range order. This forms the basis of the definitions of 'crystalline solids' and the 'amorphous solids'.

A solid is said to be* crystalline *if its various constituent particles (i.e. ions, atoms or molecules) are arranged in a definite geometric pattern in three dimensional space so that there is short range as well as long range order of the constituent particles.* On the other hand, *a solid is said to be* amorphous *if there is no regular arrangement of its constituent particles or at the most there is only a short range order of its constituent particles.

(*ii*) **Melting points.** The crystalline substances possess sharp melting points whereas the amorphous substances melt gradually over a temperature range.

(*iii*) **Isotropy and Anisotropy.** In case of amorphous substances, properties like electrical conductivity, refractive index, thermal expansion etc. are identical in all directions just as in case of gases or liquids. This property is called *isotropy* and the substances showing this property are called isotropic. On the other hand, in case of crystalline substances, the properties mentioned above have different values in different directions. This type of behaviour is called *anisotropy* and the substances exhibiting this type of behaviour are called anisotropic. Thus whereas amorphous substances are isotropic in nature, the crystalline substances are anisotropic. The anisotropy exhibited by crystalline substances is obviously due to the fact that in making measurements in different directions, different types of particles fall on the way, as shown in Fig. 2.35.

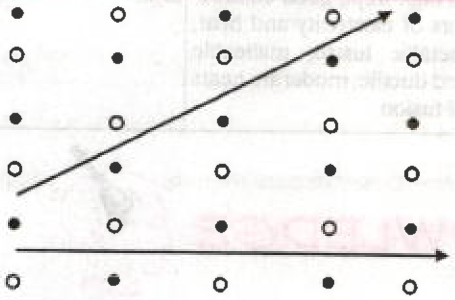


FIGURE 2.35. Anisortopy exhibited by crystalline substances.

(*iv*) **Cleavage with a knife.** A crystalline solid on being cut with a sharp knife gives a clean cleavage whereas an amorphous solid undergoes an irregular breakage as shown in Fig. 2.36.

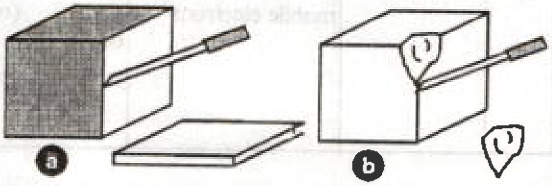


FIGURE 2.36. (a) A crystalline solid undergoes a clean cleavage (b) An amorphous solid undergoes an irregular cut.

Thus the main points of difference between a crystalline solid and an amorphous solid may be summed up as follows :

CRYSTALLINE SOLID	AMORPHOUS SOLID
(*i*) The constituent particles are arranged in a regular fashion containing short range as well as long range order.	(*i*) The constituent particles are not arranged in any regular fashion ; there may be at the most some short range order only.
(*ii*) They have sharp melting points.	(*ii*) They melt over a range of temperature.
(*iii*) They are anisotropic.	(*iii*) They are isotropic.
(*iv*) They undergo a clean cleavage.	(*iv*) They undergo an irregular cut.

In fact, only the crystalline solids are the true solids whereas *amorphous solids are considered to be highly supercooled liquids of very high viscosity and are called* **pseudo-solids.** This is supported by the fact that the glass of the window panes of some very old houses are found to be thicker at the bottom than at the top, showing some fluidity possessed by glass.

Further it may be pointed out that due to short range order possessed by amorphous solids, small parts of the amorphous solid may be crystalline while the rest may be non-crystalline. These crystalline parts of the amorphous solids are called **crystallites.**

2.18. Classification of Crystalline Solids

Based upon the nature of the constituent particles and the binding forces present between them, the crystalline solids are further classified into different types as listed in the Table 2.3 below :

TABLE 2.3. Classification of crystalline solids into different types

S. No.	CRYSTAL TYPE	CONSTITUENT PARTICLES	MAIN BINDING FORCES	PROPERTIES	EXAMPLES
1.	Ionic	Positive and negative ions arranged in a definite order	Strong electrostatic forces of attraction	Brittle, high m.p., good conductors in the aqueous solution or fused state, high heats of fusion	Salts like NaCl, KNO_3, LiF, $BaSO_4$, BaO, CaF_2 etc.
2.	Molecular	Small molecules	van der Waal's forces	Soft, low m.p., volatile, electrical insulators, poor thermal conductors, low heats of fusion	Solid CO_2 (dry ice), CH_4, wax, iodine, ice, sulphur (S_8), phosphorus (P_4).
3.	Covalent	Atoms chemically bound together in the form of a network	Covalent bond forces	Very hard, high m.p., poor conductors of heat and electricity, high heats of fusion	Diamond, silicon carbide, silica, quartz.
4.	Metallic	Positive ions and mobile electrons	Electrical attractions (metallic bond)	Very soft to very hard, low to high m.p., good conductors of electricity and heat, metallic lustre, malleable and ductile, moderate heats of fusion	All metals and some alloys.

ADD TO YOUR KNOWLEDGE

1. Ionic solids do not conduct electricity in the solid state as ions are not free to move.
2. Ionic solid is a three dimensional arrangement of cations and anions. It is just a cluster (aggregate) of ions which on the whole is electrically neutral.

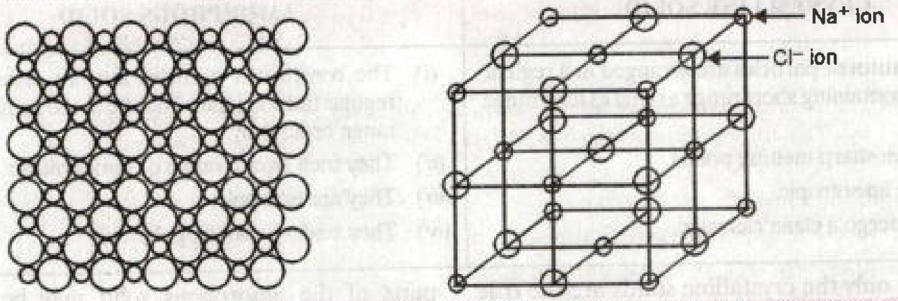


FIGURE 2.37. Clustering of ions to form an ionic solid, like NaCl.

3. A covalent solid is a giant molecule having a three dimensional network of covalent bonds *e.g.* structure of diamond is shown in Fig. 2.38 on the next page.
4. The valence electrons of a metal atom are free electrons (as force of attraction on them by the nucleus is minimum). Leaving valence electrons, the remaining portion is a positive ion, called "kernel". The free mobile electrons hold the kernels together.

The simultaneous attraction between the kernels and the mobile electrons which hold the kernels together is called **metallic bond.**

ADD TO YOUR KNOWLEDGE CONTD.

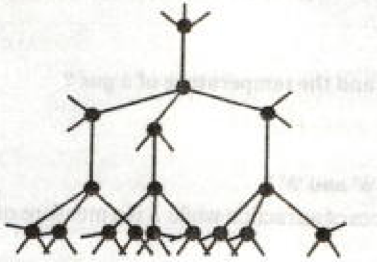


FIGURE 2.38. Structure of diamond.

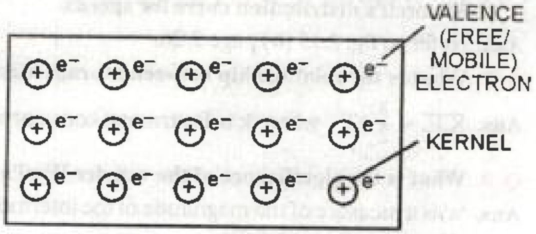


FIGURE 2.39. Electron sea model of metallic bond.

Thus metallic bond spreads over the whole crystal and is non- directional. This model is called *"electron sea model."* (Fig. 2.39)

5. The order of melting points of different types of crystalline solids is as follows :

Covalent	>	Ionic	>	Metalic	>	Molecular
(~ 4000 K)		(~ 1000 K)		(880-1000 K)		(273-600 K)

6. The melting point of a substance is a measure of the magnitude of the binding force among the constituent particles. For example, the order of melting points and hence that of the binding force for a few substances are given below :

	O_2	<	N_2	<	C_2H_5OH	<	H_2O	<	C_6H_6	<	Na	<	NaCl
M. pts. (K)	55		63		159		273		278		371		1077
					Molecular crystals						Metallic		Ionic

Conceptual Questions

Q. 1. Arrange solid, liquid and gas in order of energy, giving reasons.

Ans. Solid < Liquid < Gas. This is because a solid absorbs energy to change into a liquid which further absorbs energy to change into a gas.

Q. 2. A gas is filled into a bulb connected to an open limb manometer. The difference in the levels of the two limbs is 2·1 cm. The atmospheric pressure is 740 mm. What is the pressure of the gas ?

Ans. 740 — 21 = 719 mm.

Q. 3. How do you convert

(*a*) pressure in atmospheres into SI units ?

(*b*) temperature in °C to temperature in °F ?

Ans. (*a*) 1 atm. = 101, 325 Pa or Nm^{-2} or 1 bar = 10^5 Pa

(*b*) $°C = \frac{5}{9}(°F - 32)$

Q. 4. What type of graph will you get when PV is plotted against P at constant temperature.

Ans. A straight line parallel to pressure axis.

Q. 5. How is the pressure of a gas related to its density at a particular temperature ?

Ans. $d = \frac{MP}{RT}$

Q. 6. How is the partial pressure of a gas in a mixture related to the total pressure of the gaseous mixture ?

Ans. Partial pressure of a gas = Mole fraction of that gas × Total pressure.

Q. 7. Represent the relative values of most probable speed, average speed and root mean square speed on Maxwell's distribution curve for speeds.

Ans. Refer to fig. 2.15 (*b*) page 2/26.

Q. 8. What is the relationship between average kinetic energy and the temperature of a gas ?

Ans. $\text{K.E.} = \frac{3}{2} kT$ where k is Boltzmann constant $= \left(\frac{R}{N_0}\right)$

Q. 9. What is the significance of the van der Waal's constants '*a*' and '*b*' ? *(N.C.E.R.T.)*

Ans. '*a*' is a measure of the magnitude of the intermolecular forces of attraction while *b* is a measure of the effective size of the gas molecules.

Q. 10. Why in case of hydrogen and helium, the compresibility factor is always greater than 1 and increases with increase of pressure ?

Ans. Refer to 'Explanation of exceptional behaviour of H_2 and He, page 2/31.

Q. 11. The van der Waal's constants for two gases are as follows :—

Gas	a (atm L^2 mol^{-2})	b (L mol^{-1})
X	1·39	0·0391
Y	3·59	0·0427

Which of them is more easily liquefiable and which has greater molecular size ?

Ans. Greater the value of '*a*', more easily the gas is liquefiable. Similarly, greater the value of '*b*', greater is the molecular size. Hence gas Y will be more easily liquefiable and will have greater molecular size.

Q. 12. Compare the rates of diffusion of $^{235}UF_6$ and $^{238}UF_6$.

Ans. Molecular mass of $^{235}UF_6 = 235 + 6 \times 19 = 349$

Molecular mass of $^{238}UF_6 = 238 + 6 \times 19 = 352$

$$\therefore \quad \frac{r_1(^{235}UF_6)}{r_2(^{238}UF_6)} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{352}{349}} = 1{\cdot}004$$

Thus $r(^{235}UF_6) : r(^{238}UF_6) = 1{\cdot}004 : 1.$

Q. 13. At a certain altitude, the density of air is 1/10th of the density of the earth's atmosphere and temperature is —10°C. What is the pressure at that altitude? Assume that air behaves like an ideal gas, has uniform composition and is at S.T.P. at the earth's surface.

Ans. $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$ or $P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$.

But $d \propto \frac{1}{V}$. Hence $P_2 = \frac{P_1 T_2}{T_1}\left(\frac{d_2}{d_1}\right) = \frac{760 \times 263}{273}\left(\frac{1}{10}\right)$ **= 73·2 mm.**

Q. 14. What would be the SI unit for the quantity pV^2T^2 / n ? *(N.C.E.R.T.)*

Ans. $\frac{(N m^{-2})(m^3)^2 (K)^2}{mol} = N m^4 K^2 mol^{-1}$

Q. 15. In terms of Charles' law explain why —273°C is the lowest temperature. *(N.C.E.R.T.)*

Ans. At —273°C, volume of the gas becomes equal to zero *i.e.* the gas ceases to exist.

Q. 16. Critical temperature for CO_2 and CH_4 are 31·1°C and —81·9°C respectively. Which of these has stronger intermolecular forces and why ? *(N.C.E.R.T.)*

Ans. Higher the critical temperature, more easily the gas can be liquefied *i.e.* greater are the intermolecular forces of attraction. Hence CO_2 has stronger intermolecular forces than CH_4.

Q. 17. What is the ratio of average kinetic energy of oxygen molecules to that of ozone molecules at 27°C ?

Ans. Average kinetic energy of any gas depends only on temperature and not upon the nature of the gas. Hence both the gases will have same average kinetic energy at 27°C *i.e.* the ratio will be 1 : 1.

Q. 18. What is the difference between total kinetic energy and translational kinetic energy ? For what type of molecules, the two are equal ?

Ans. Total kinetic energy is the sum of translational, vibrational and rotational kinetic energies. The total kinetic energy is equal to the translational kinetic energy for monoatomic gases (He, Ne etc.) as they do not possess vibrational and rotational motion but have only translational motion.

Q. 19. Out of N_2 and NH_3, which one will have greater value of 'a' and which one will have greater value of 'b' ?

Ans. (*i*) As NH_3 is more easily liquefiable (due to hydrogen bonding), intermolecular forces of attraction are stronger than in N_2. Hence NH_3 will have greater value for '*a*'.

(*ii*) As NH_3 molecule is larger in size than N_2, hence NH_3 will have greater value for '*b*'.

(For NH_3, $a = 4{\cdot}17\ L^2\ atm\ mol^{-2}$, $b = 0{\cdot}0371\ L\ mol^{-1}$

For N_2, $a = 1{\cdot}39\ L^2\ atm\ mol^{-2}$, $b = 0{\cdot}0319\ L\ mol^{-1}$)

Q. 20. What would have happened to the gas if the molecular collisions were not elastic ?

Ans. On every collision, there would have been loss of energy. As a result, the molecules would have slowed down and ultimately settle down in the vessel.

Q. 21. CO_2 is heavier than O_2 and N_2 gases present in the air but it does not form the lower layer of the atmosphere. Why ?

Ans. Gases possess the property of diffusion which is independent of the force of gravitation. Due to diffusion, the gases mix into each other and remain almost uniformly distributed in the atmosphere.

Q. 2 N_2O and CO_2 have the same rate of diffusion under same conditions of temperature and pressure. Why ?

Ans. Both have same molar mass (= 44 g mol^{-1}). According to Graham's law of diffusion, rates of diffusion of different gases are inversely proportional to the square root of their molar masses under same conditions of temperature and pressure.

Q. 2 Why liquids have a difinite volume but no definite shape ?

Ans. This is because the intermolecular forces are strong enough to hold the molecules together but not so strong as to fix them into definite positions (as in solids). Instead, they possess fluidity and hence no definite shape.

Q. 2 At a particular temperature, why vapour pressure of acetone is less than that of ether ?

Ans. This is because the intermolecualr forces of attraction in acetone are stronger than those present in ether.

Q. 25 A liquid is transferred from a smaller vessel to a bigger vessel at the same temperature. What will be the effect on the vapour pressure ?

Ans. No effect as it depends only on the nature of the liquid and temperature.

Q. Why vegetables are cooked with difficulty at a hill station ?

Ans. The atomopheric pressure is less and so the boiling point is lowered.

Q. What is the approximate relationship between heat of vaporisation and boiling point of a liquid ?

Ans. $\Delta H_{vap.} / T_b = 21\ cal\ K^{-1}\ mol^{-1}$ (Trouton's rule).

Q. What is the effect of temperature on

(*i*) Surface tension and (*ii*) Viscosity ?

Ans. Both decrease with increase of temperature.

Q. Why falling liquid drops are spherical ?

Ans. This is due to property of surface tension possessed by the liquids. This makes the surface area minimum. For a given volume, sphere has the minimum surface area.

Q. What happens if a liquid is heated to the critical temperature of its vapours ?

Ans. The meniscus between the liquid and the vapour disappears (surface tension of the liquid becomes zero).

Q. 31. Why liquids diffuse slowly as compared to gases?

Ans. In liquids, the molecules are less free than in a gas *i.e.* the intermolecular forces (van der Waal's forces) in a liquid are greater than in a gas.

Q. 32. Why amorphous solids are considered to be supercooled liquids ?

Ans. (*i*) Like liquids, amorphous solids are *isotropic*

(*ii*) Like liquids, they possess *fluidity*.

Q. 33. Why urea has a sharp melting point but glass does not ?

Ans. Urea is a crystalline solid whereas glass is amorphous. Crystalline solids have sharp melting points whereas amorphous solids do not possess sharp melting point.

Very Short Answer Questions CARRYING 1 MARK

Q. 1. Which state of matter has a definite volume but no definite shape ?

Ans. Liquid.

Q. 2. What is the equation of state of an ideal gas for n moles ?

Ans. $PV = nRT$.

Q. 3. What is the value of the gas constant in S.I. units?

Ans. $8{\cdot}314\ JK^{-1}\ mol^{-1}$.

Q. 4. What is compressibility factor ?

Ans. $Z = \frac{PV}{nRT}$

Q. 5. What is the equation of state for real gases ?

Ans. van der Waal equation, $\left(P + \frac{a}{V^2}\right)(V-b) = RT$

Q. 6. Why a liquid boils at a lower temperature at the top of a mountain than at sea level ?

Ans. This is because the pressure at the top of a mountain is low.

Q. 7. What are the S.I. units of surface tension ?

Ans. Nm^{-1}.

Q. 8. What are the units of coefficient of viscosity ?

Ans. Poise.

Q. 9. What is SI unit of coefficient of viscosity ? How is it related to poise ?

Ans. SI unit $= kg\,m^{-1}\,s^{-1}$

Poise $= 1\ g\ cm^{-1}\,s^{-1}$

$\therefore$ 1 poise $= \frac{1}{10}$th of SI unit.

Q. 10. Why ice has a sharp melting point whereas glass melts over a range of temperature ? ***(N.C.E.R.T.)***

Ans. Ice is a crystalline solid whereas glass is an amorphous solid.

Q. 11. What is the binding force between molecules, if a substance is a gas under ordinary conditions of temperature and pressure ? ***(B.I.T. Ranchi 1990)***

Ans. van der Waal's forces

Short Answer Questions CARRYING 2 or 3 MARKS

Sec. 2.1. to 2.3.

1. What is the difference between a barometer and a manometer ?
2. On the basis of intermolecular forces and thermal energy, explain why
   (*i*) a solid has rigidity but liquids do not have rigidity ?
   (*ii*) gases have high compressibility but liquids and solids have poor compressibility ?
3. How is the pressure of a gas measured ?

Sec. 2.4.

4. Define Boyle's law. How is it represented mathematically ?
5. What type of curves are obtained when at constant temperature we plot
   (*i*) P vs 1/V (*ii*) PV vs P (*iii*) V vs P
6. On the basis of Boyle's law explain why mountaineers carry oxygen cylinders with them.
7. Define Charles' law. Give its mathematical formulae.
8. Define Absolute zero. Can this temperature be attained in actual practice ? Give reason for your answer.
9. Derive the value of gas constant in S.I. units.
10. Define Dalton's law of partial pressures. Using this law, how is the pressure of dry gas determined ?
11. Define Graham's law of diffusion.
12. Derive the relationship between pressure, temperature and density of a gas (*i.e.* $M = d\,RT/P$).

Sec. 2.5.

13. List the important postulates of kinetic theory of gases.

Sec. 2.6. to 2.8.

14. Define most probable speed, average speed and root mean square speed. How are they related to each other ?
15. Write kinetic gas equation. How does Boyle's law follow from it ?
16. Write kinetic gas equation. How does Charles' law follow from it ?

Sec. 2.9. to 2.10.

17. Starting from kinetic gas equation, prove that the average kinetic energy of a gas is directly proportional to its absolute temperature.
18. What is 'compressibility factor' ? What is its value for 'an ideal gas' ? How does it help to understand the extent of deviation of a gas from ideal behaviour?
19. Why do real gases show deviation from ideal behaviour ? Write van der Waal's equation for *n* moles of a gas.
20. What are the units of van der Waal's constants '*a*' and '*b*' ? What is their significance ?

Sec. 2.11. to 2.13.

21. Why is the effect of temperature more important for the liquefaction of gases ? Define critical temperature and critical pressure.
22. Define Joule-Thomson effect. Why hydrogen and helium show exceptional behaviour ?
23. Briefly describe the importance of critical temperature. How can it be correlated with van der Waal's constant '*a*' ?

Sec. 2.14. to 2.15.

24. Explain the statement 'Liquid state is intermediate between the gaseous state and the solid state.'
25.
26. Give reasons for the following :—
   (*i*) Liquids have a definite volume but no definite shape.
   (*ii*) Liquids have higher density than gases.
   (*iii*) Liquids are much less compressible than gases.
   (*iv*) Liquids possess fluidity.
27. Define vapour pressure, boiling point and heat of vaporisation.
28. What is difference between Boiling and Evaporation ?
29. Explain the effect of temperature on the following:
   (*i*) Surface tension (*ii*) Viscosity
   (*iii*) Vapour pressure (*iv*) Density.
30. Give reasons for the following :

(*i*) Boiling point of a liquid rises on increasing pressure.

(*ii*) Drops of a liquid assume a spherical shape.

(*iii*) The level of mercury in a capillary tube is lower than the level outside when a capillary tube is inserted in mercury.

(*iv*) Tea or coffee is sipped from the saucer when it is quite hot.

Sec. 2.16. **31.** What are the important characteristics of a solid ?

Sec. 2.17. **32.** List the points of difference between a crystalline solid and an amorphous solid.

Sec. 2.18. **33.** Classify the following crystalline solids into different types, giving reasons for your answer :
Diamond, Copper, Solid CO_2 (dry ice), $BaSO_4$

Long Answer Questions CARRYING 5 or more MARKS

Sec. 2.1. **1.** List the main points of difference between a solid, a liquid and a gas.

Sec. 2.2. **2.** On the basis of intermolecular forces and thermal energy, explain why substances exist in three different states.

Sec. 2.3. **3.** How are the following measured ?
(*i*) atmospheric pressure (*ii*) pressure of a gas.

Sec. 2.4. **4.** State and explain Boyle's law. How is the law verified graphically ? What is the significance of this law to the mountaineers?

5. State and explain Charles' law. How does it lead to the concept of 'absolute zero' ? How is this law made use of in the meteorological observations ?

6. Briefly explain Pressure-Temperature law.

7. What is ideal gas equation ? How can it be derived? Also express it in terms of density of the gas.

8. Discuss the nature of the gas constant 'R'. Derive its value in terms of different units.

9. State and explain Dalton's law of partial pressures. How is this law applied in the determination of pressure of dry gas from that of the moist gas ?

10. Define Graham's law of diffusion. Give its mathematical formulation.

Sec. 2.5. **11.** (*a*) What are the important postulates of kinetic molecular theory of gases ?
(*b*) Write kinetic gas equation. What do different symbols signify ?
or Briefly explain the Dynamic Particle Model or the Microscopic model of a gas.

Sec. 2.6. **12.** (*a*) Write a short note on "Maxwell's distribution of speeds".
(*b*) Define most probable speed, average speed and root mean square speed. How are they related to each other ?

Sec. 2.7. to 2.8. **13.** Write kinetic gas equation. Deduce following gas laws from it :
(*i*) Boyle's law (*ii*) Charles' law (*iii*) Dalton's law of partial pressures.

14. List the postulates of Kinetic-molecular theory of gases. On the basis of these postulates, explain the following gas laws:
(*i*) Boyle's law (*ii*) Charles' law (*iii*) Dalton's law of partial pressures.

Sec. 2.9. **15.** Starting from kinetic gas equation, derive a relationship between average kinetic energy and absolute temperature of a gas.

Sec. 2.10. **16.** What are ideal and real gases ? What is compressibility factor ? How does it help in understanding the deviation of real gases from ideal behaviour ?

17. Why do real gases deviate from ideal behaviour ? Write the equation of state for real gases (van der Waal's equation).

18. Starting from van der Waal's equation explain, the behaviour of real gases under different conditions of temperature and pressure.

19. How can van der Waal's equation explain the exceptional behaviour of hydrogen and helium ?

Sec 2.11 to 2.13. **20.** Briefly explain Linde's process for liquefaction of gases.

21. Briefly explain Claude's process for liquefaction of gases.

Sec. 2.14. to 2.15. **22.** What are the main postulates of 'Kinetic Molecular Theory of Liquids ? On the basis of this model how can you explain the following properties of liquids ?

(*i*) Volume (*ii*) Density (*iii*) Compressibility (*iv*) Diffusion.

23. Briefly explain the term "vapour pressure". What are the factors on which the vapour pressure of a liquid depends ?

24. What is surface tension ? What are its units ? What is the effect of temperature on surface tension ?

25. Briefly explain the term 'Viscosity'. Define 'coefficient of viscosity'. What are its units ? What is the effect of temperature on the viscosity of a liquid ?

Sec. 2.16. to 2.17. **26.** What are the general characteristics of solids ? How do amorphous solids differ from crystalline solids ?

Sec. 2.18. **27.** Based upon the nature of the constitutent particles and the binding forces between them, how are the crystalline solids classified into different types ? Give the important properties and examples of each type.

COMPETITION FOCUS

ADDITIONAL USEFUL INFORMATION

1. Critical constants in terms of van der Waal's constants. The critical constants are related to van der Waal's constants by the following expressions $P_c = a / 27\,b^2,\ T_c = 8\,a / 27\,Rb,\ V_c = 3\,b$.

Further, they are related to each other as $P_cV_c = \frac{3}{8}RT_c$.

Alternatively, knowing critical constants, van der Waal's constants can be calculated, using the above expressions.

2. Boyle temp. and critical temp. in terms of van der Waal's constants $T_B = \frac{a}{Rb}$, $T_C = \frac{8a}{27\,Rb}$.

Thus $T_B > T_C$

3. Inversion temperature. Every gas has a definite temperature at which the gas shows neither heating effect nor cooling effect when allowed to expand adiabatically according to Joule-Thomson effect. Above this temperature, the gas shows heating effect and below this temperature, the gas shows cooling effect. This temperature is called inversion temperature. Most of the gases have high inversion temperature (much higher than room temperature). Hydrogen and helium have low inversion temperatures. Inversion temperature can be calculated from van der Waal's constants as follows :

$$T_i = \frac{2\,a}{R\,b}$$

4. Molecular diameter. When the molecules of a gas come close to each other, a stage comes when the repulsion starts between them. The distance between the centres of the molecules when they are closest to each other *i.e.* just before the repulsion starts between them is called molecular diameter (σ).

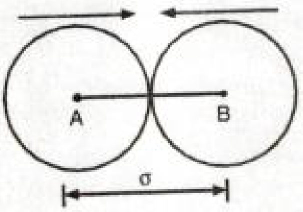


FIGURE 2.40. Molecular diameter, σ

5. Collision frequency. The number of collisions which take place in one second among the molecules present in 1 cc of the gas is called collision frequency. It is denoted by Z.

6. Collision number. The number of collisions which a single molecule undergoes with other molecules in one second is called collision number. It is denoted by N_C.

ADDITIONAL USEFUL INFORMATION contd.

7. Expressions for collision number (N_C) and collision frequency (Z) $N_C = \sqrt{2}\,\pi\, v\, \sigma^2 n$

where v = average speed, σ = molecular diameter and n = no. of molecules/cc of the gas

Collisions among all the molecules = $N_C \times n$

As each collision involves two molecules, $Z = \dfrac{N_C \times n}{2} = \dfrac{1}{\sqrt{2}}\pi\, v\, \sigma^2 n^2$

Putting $v = \sqrt{\dfrac{8RT}{\pi M}}$, $Z = 2\sigma^2 n^2 \sqrt{\dfrac{\pi RT}{M}}$

Note that with increase in temperature, v increases and with increase in pressure n increases. So in both cases, Z increases.

8. Mean free path. The distance travelled by a molecule between any two successive collisions is called free path. The average of these distances is called the mean free path $\left(l = \dfrac{l_1 + l_2 + l_3 + \ldots}{n}\right)$.

Mathematically, it is given by $\bar{l} = \dfrac{1}{\sqrt{2}\,\pi\,\sigma^2 N}$

where σ = molecular diameter,

N = number of molecules of the gas per unit volume

But for n moles of an ideal gas,

$PV = nRT$

or number of moles per unit volume, $\dfrac{n}{V} = \dfrac{P}{RT}$

$\therefore$ Number of molecules per unit volume $= \dfrac{PN_0}{RT}$

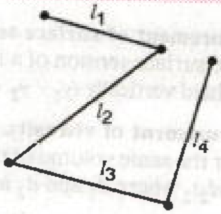


FIGURE 2.41. Free paths.

Putting $N = PN_0/RT$, the above equation becomes $\bar{l} = \dfrac{1}{\sqrt{2}\,\pi\,\sigma^2} \dfrac{RT}{PN_0}$

Thus $\bar{l} \propto T$ and $\propto 1/P$

9. Logarithmic plots for Boyle's law and Charles' law.

According to Boyle's law, $PV = \text{constant}$

$\therefore$ $\log P + \log V = \text{constant}$ or $\log P = -\log V + \text{constant}$

Hence the plot of log P vs log V is as shown in Fig. 2.42.

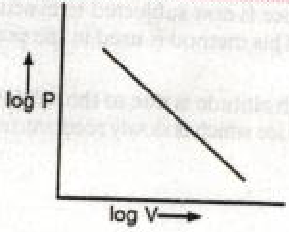


FIGURE 2.42. Plot of log P vs log V.

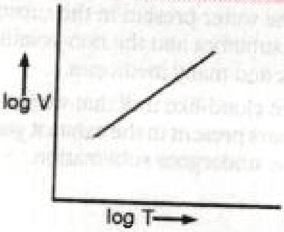


FIGURE 2.43. Plot of log V vs log T.

According to Charles' law, $\dfrac{V}{T} = \text{const.}$

$\therefore$ $\log V - \log T = \text{const.}$ or $\log V = \log T + \text{const.}$

Hence plot of log V vs log T will be as shown in Fig. 2.43.

ADDITIONAL USEFUL INFORMATION contd.

10. Amagat's law of partial volumes. This law is similar to Dalton's law of partial pressures. According to this law, "the total volume of a mixture of non-reacting gases is the sum of their partial volumes where partial volume of a gas is the volume occupied by that gas at the same temperature and at the pressure of the mixture." Mathematically

$$V_T = v_1 + v_2 + v_3 + \cdots$$

11. Average molecular mass of a gaseous mixture.

$$\overline{M}_{mix} = \frac{\Sigma n_i M_i}{\Sigma n_i} = \Sigma x_i M_i$$

where n_i is the number of moles and M_i is the molecular mass of component i (x_i is mole fraction of the component i).

12. Liquid Crystals. There are certain organic compounds which on heating melt to give a turbid (milky) liquid which on further heating becomes clear. The reverse happens on cooling the clear liquid. The turbid liquid is found to be anisotropic, a property possessed by crystalline solids. Hence these turbid liquids are called liquid crystals.

13. Measurement of surface tension. The apparatus used is called **stalgmometer.** It is based upon the principle that the surface tension of a liquid is directly proportional to the mass of the spherical drop falling from a capillary tube held vertically ($\gamma_1 / \gamma_2 = m_1 / m_2$)

14. Measurement of viscosity. The apparatus used is called **Ostwald viscometer.** It is based upon the principle that for the same volume of the two liquids flowing from the same height and through the same capillary $\eta_1 / \eta_2 = d_1 t_1 / d_2 t_2$ where d_1 and d_2 are densities and t_1 and t_2 are their times of flow.

15. Clausius-Clapeyron equation. It gives the variation of vapour pressure of a liquid with temperature. The equation is

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2 \cdot 303\, R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

where ΔH_v = enthalpy of vaporisation of the liquid.

16. Vapour pressure of solids. Like liquids, the solids also evaporate and hence possess vapour pressure. This is because in a crystalline solid, the molecules keep on vibrating about their mean positrons and hence keep on colliding with the neighbouring molecules. As a result, a redistribution of kinetic energy takes place between them. The molecules with higher kinetic energy on the surface leave the solid and come in the space above it. The process is called *sublimation*.

17. Freeze drying. Substances like NH_4Cl, iodine, camphor, solid CO_2 etc. sublime at ordinary temperature and pressure. However, snow sublimes when the surrounding temperature is below 0°C. This property is used in the process called 'freeze drying'. Substances containing water vapour are cooled below —10°C at atmospheric pressure. All the water present in the substance freezes to ice. The substance is now subjected to evacuation. As a result, water sublimes and the non-volatile components are left behind. This method is used in the preparation of powder milk and many medicines.

The white cloud-like trail that we see coming out of a jet flying at high altitude is due to the solidification of the water vapours present in the exhaust gases directly into microcrystalline ice which is slowly reconverted directly into vapours *i.e.* undergoes sublimation.

C.B.S.E.-P.M.T. (MAINS) SPECIAL

A. SUBJECTIVE QUESTIONS

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

Ans. Consider two molecules A and B. Taking the molecules to be spherical, if r is the radius of the molecules, then the distance of closest approach between the two molecules $= 2r$ (as shown in Fig. 2.44).

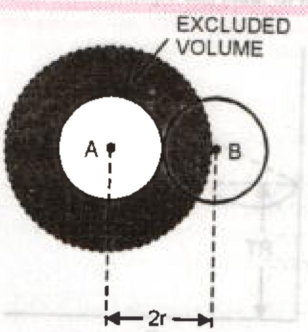


FIGURE 2.44.

Since the molecules cannot come closer than distance $2r$, the excluded volume for a pair of molecules = volume of sphere of radius $2r$

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

∴ Excluded volume per molecule (b)

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

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

Q. 2. Draw the plot of

(i) Log P vs Log V at constant temperature.

(ii) Log V vs Log T at constant pressure.

Ans. Refer to point 9, page 2/55.

Q. 3. Give a reasons for the following :

(i) The size of weather balloon becomes larger and larger as it ascends into higher altitudes.

(ii) Tyres of automobiles are inflated to lesser pressure in summer than in winter.

Ans. (*i*) As we go to higher altitudes, the atmospheric pressure decreases. Then the pressure outside the balloon decreases. To regain equilibrium with the external pressure, the gas inside expands to decrease its pressure. Hence the size of the balloon increases.

(*ii*) In summer, due to higher temperature, the average kinetic energy of the air molecules inside the tyre increases *i.e.* molecules start moving faster. Hence the pressure on the walls of the tube increases. If pressure inside is not kept low at the time of inflation, at higher temperature, the pressure may become so high that the tyre may burst.

Q. 4. Give reason for the following :

(i) Sodium metal is soft with low melting point whereas sodium chloride is hard with high melting point.

(ii) Diamond has a very high melting point.

(iii) Copper is malleable and ductile but brass is hard and brittle.

Ans. (*i*) In sodium metal, the positively charged Na^+ ions (kernels) are held together by weak metallic bonds whereas or NaCl, the oppositely charged Na^+ and Cl^- ions are held together by strong electrostatic forces of attraction. Hence sodium metal is soft with low melting point whereas NaCl is hard with high melting point.

(*ii*) Diamond is a covalent solid and is a giant molecule with three dimensional network of covalent bonds. Hence it has very high melting point.

(*iii*) Copper is a metal but brass is an alloy of copper and zinc. In copper, the layers of kernels can slip over each other. As a result, it is malleable and ductile. In brass, as some copper atoms are replaced by zinc atoms, the properties change. The layers cannot slip over each other. Hence it becomes hard and brittle.

Q. 5. Using the equation of state pV = n RT, show that at a given temperature, density of a gas is proportional to the gas pressure, p.

(N.C.E.R.T.)

Ans. Refer to page 2/13.

Q. 6. The molecular speeds of gaseous molecules are analogous to those of rifle bullets. Then why is the odour of a gas not detected so fast ?

Ans. Though the molecules of a gas travel at high speeds but they do not travel in straight lines in one direction like bullets. As they travel, they collide with the molecules of the gases present in the air. As a result, they are deflected. Thus, they follow a zig-zag path *i.e.* the net distance travelled in a particular direction is quite small in a given time. That is why the odour is not detected so fast.

Q. 7. Arrange the following in order of increasing density.

Oxygen at 25°C, 1 atm ; Oxygen at 0°C, 2 atm ; Oxygen at 273°C, 1 atm

(M.L.N.R. Allahabad 1992)

Ans. $d \propto \frac{1}{V}$ and $V = \frac{RT}{P}$

V for O_2 at 25°C, 1 atm

$$= \frac{R \times 298}{1} = 298\ R$$

V for O_2 at 0°C, 2 atm

$$= \frac{R \times 273}{2} = 136 \cdot 5\ R$$

V for O_2 at 273°C, 1 atm

$$= \frac{R \times 446}{1} = 446\ R$$

Hence increasing order of density will be O_2 at 273°C, 1 atm ; O_2 at 25°C, 1 atm ; O_2 at 0°C, 2 atm.

Q. 8. Why dry air is heavier than moist air ?

Ans. Average mol. mass of dry air

$$= \frac{\%\text{ of } N_2 \times 28 + \%\text{ of } O_2 \times 32}{100}$$

Average mol. mass of moist air

$$= \frac{\%\text{ of } N_2 \times 28 + \%\text{ of } O_2 \times 32 + \%\text{ of } H_2O \times 18}{100}$$

Evidently average mol. mass of dry air is more and so is its density ($d = M / V$).

Q. 9. One way of writing the equation of state for real gases is

$$PV = RT\left[1 + \frac{B}{V} + \ldots\right]$$

where B is a constant. Derive an approximate expression for B in terms of the van der Waal's constants *a* and *b* ***(I.I.T. 1997)***

Ans. According to van der Waal's equation

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

$$\Rightarrow \quad P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$\Rightarrow \quad PV = \frac{RTV}{V - b} - \frac{a}{V}$$

$$\text{or} \quad PV = RT\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V}$$

$$= RT\left(1 + \frac{b}{V}\right) - \frac{a}{V}$$

(Neglecting higher powers of b/V)

$$\Rightarrow \quad PV = RT\left(1 + \frac{b}{V} - \frac{a}{VRT}\right)$$

$$= RT\left[1 + \frac{1}{V}\left(b - \frac{a}{RT}\right)\right]$$

Comparing with the given form of the equation,

$$B = b - \frac{a}{RT}$$

Q. 10. For a real gas obeying van der Waal's equation, a graph is plotted between PV_m (y-axis) and P (x-axis) where V_m is the molar volume. Find y-intercept of the graph. ***(I.I.T. 2004)***

Ans. For a real gas, the plot of PV_m vs P can be of the type A or B but at the point of intercept, P = 0 and at any low pressure, van der Waal's equation reduces to ideal gas equation

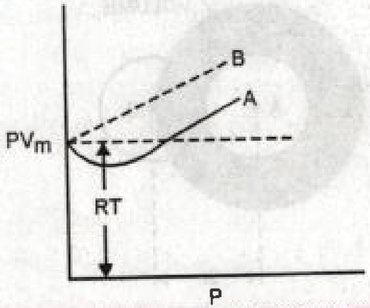


FIGURE 2.45.

$$PV = n\,RT \quad \text{or} \quad PV_m = RT$$

Hence y-intercept of graph will be = RT

Q. 11. On which factors will the rate of diffusion of a gas depend ? ***(West Bengal J.E.E. 2004)***

Ans. Rate of diffusion of a gas depends upon

(*i*) density or molecular mass of the gas

(*ii*) pressure of the gas

(*iii*) temperature of the gas

At constant temperature, $r \propto P \times \frac{1}{\sqrt{d}}$

B. PROBLEMS

Problem 1. **Assuming oxygen molecule to be spherical in shape, calculate the volume of a single molecule of oxygen if its radius is 150 pm. Also calculate the percentage of empty space in one mole of the gas at S.T.P.**

Solution. As oxygen molecule is spherical, therefore, volume of one molecule $= \frac{4}{3}\pi r^3$

$$= \frac{4}{3} \times \frac{22}{7}(150 \times 10^{-10}\ \text{cm})^3$$

$$= 1 \cdot 41 \times 10^{-23}\ \text{cm}^3$$

To calculate the empty space in 1 mole of O_2 molecules, let us first calculate the volume occupied by 1 mole of molecules *i.e.* $6 \cdot 022 \times 10^{23}$ molecules. This will be $= (6 \cdot 022 \times 10^{23}) \times (1 \cdot 41 \times 10^{-23}\ \text{cm}^3) = 8 \cdot 49\ \text{cm}^3$.

But volume occupied by 1 mole of molecules at S.T.P. = 22400 cm^3

$\therefore$ Empty space = 22400 − 8·49 cm^3

$= 22391\cdot51\ cm^3$

$\therefore$ %age of empty space

$$= \frac{22391\cdot51}{22400} \times 100 = 99\cdot96\%.$$

Problem 2. **The boiling point of n-hexane is 68·9°C. Calculate its approximate critical temperature.**

Solution. According to Guldberg's rule, for a liquid $T_b \approx \frac{2}{3} T_c$. Hence $T_c \approx \frac{3}{2} T_b = \frac{3}{2}(68\cdot9 + 273)$ K

$= 512\cdot85$ K $= 512\cdot85 - 273$°C

$= 239\cdot85$°C.

Problem 3. **Assuming CO_2 to be van der Waal's gas, calculate its Boyle temperature. Given $a = 3\cdot59\ L^2$ atm mol^{-2} and $b = 0\cdot0427$ L mol^{-1}.**

Solution. Boyle temperature in terms of van der Waal's constants is $T_B = \frac{a}{Rb}$. Hence

$$T_B = \frac{3\cdot59\ L^2\ \text{atm mol}^{-2}}{(0\cdot0821\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (0\cdot0427\ \text{L mol}^{-1})}$$

$= 1024$ K.

Problem 4. **In a hospital, an oxygen cylinder holds 10 L of oxygen at 200 atm pressure. If a patient breathes in 0·50 mL of oxygen at 1·0 atm with each breath, for how many breaths the cylinder will be sufficient. Assume that all the data is at 37°C.**

Solution. 10 L at 200 atm = ? L at 1 atm (temperature remaining constant)

$P_1 V_1 = P_2 V_2$

$200 \times 10 = 1 \times V_2$ or $V_2 = 2000$ L

Number of breaths

$$= \frac{\text{Total volume}}{\text{Volume consumed per breath}}$$

$$= \frac{2000\ L}{0\cdot5 \times 10^{-3}\ L} = 4 \times 10^6$$

Problem 5. **A cylinder of 20·0 L capacity contains 160 g of oxygen gas at 25°C. What mass of oxygen must be released to reduce the pressure of the cylinder to 1·2 atm ?**

Solution. Number of moles of oxygen gas present initially in the cylinder $= \frac{160\ g}{32\ g\ mol^{-1}} = 5$ moles

(Molar mass of $O_2 = 32\ g\ mol^{-1}$)

To calculate the number of moles now present, we have

P = 1·2 atm, T = 298 K, V = 20·0 L

Applying the relation, PV = *n* RT, we have

$$n = \frac{PV}{RT} = \frac{1\cdot2\ \text{atm} \times 20\cdot0\ L}{0\cdot0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 298\ K}$$

$= 0\cdot98$ mol

$\therefore$ Number of moles of O_2 required to be released

$= 5 - 0\cdot98 = 4\cdot02$ mol

or Mass of O_2 required to be released

$= 4\cdot02 \times 32\ g = 128\cdot64\ g$

Problem 6. **50 litre of dry N_2 is passed through 36 g H_2O at 27°C. After the passage of the gas, the mass of water was reduced to 34·80 g. Calculate the aqueous tension of water at 27°C.**

Solution. Water carried away by N_2 gas $= 36 - 34\cdot80 = 1\cdot20\ g$

As this water is carried away by 50 L of N_2 gas, this means that volume occupied by water vapours = 50 L. Thus now we have

$n = \frac{1\cdot20}{18} = 0\cdot0667$ mol, V = 50 L, T = 300 K, P = ?

Applying the gas equation, PV = *n* RT

$$P = \frac{n\,RT}{V}$$

$$= \frac{0\cdot0667\ \text{mol} \times 0\cdot0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 300\ K}{50\ L}$$

$= 0\cdot03286$ atm $= 0\cdot03286 \times 760$ mm

$= 24\cdot97$ mm.

Problem 7. **A 5-L vessel contains 1·4 g of nitrogen. When heated to 1800 K, 30% of molecules are dissociated into atoms. Calculate the pressure of the gas at 1800 K.**

Solution.	N_2	$\rightleftharpoons$	2 N
Initial moles	$\frac{1\cdot4}{28}$ $= 0\cdot05$		0
Moles after disso.	$0\cdot05 - \frac{30}{100} \times 0\cdot05$ $= 0\cdot05 - 0\cdot015$ $= 0\cdot035$		$2 \times 0\cdot015$ $= 0\cdot030$

$\therefore$ Total number of moles $= 0\cdot035 + 0\cdot030$

$= 0\cdot065$

i.e. $n = 0\cdot065$ mol, V = 5 L,

T = 1800 K, P = ?

Applying PV = *n* RT, we get

$$P = \frac{n\,RT}{V}$$

$$= \frac{0\cdot665\ \text{mol} \times 0\cdot0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 1800\ K}{5\ L}$$

$= 1\cdot92$ atm

Problem 8. **The volume expansivity of a gas under constant pressure is 0·0037. Calculate its volume at —100°C if its volume at 100°C is 685 cm^3.**

Solution. Volume expansivity of a gas means increase or decrease in volume per degree rise or fall in temperature of its volume at 0°C.

$$V_t = V_0 + 0\cdot0037 \times V_0 \times t$$

$$= V_0(1 + 0\cdot0037\,t)$$

At 100°C,

$$V_{100°C} = V_0(1 + 0\cdot0037 \times 100)$$

$$= 685 \text{ cm}^3 \qquad (Given)$$

or $$V_0 = \frac{685}{1\cdot37} = 500 \text{ cm}^3$$

At —100°C,

$$V_{-100°C} = 500\,[1 + 0\cdot0037 \times (-100)]$$

$$= 315 \text{ cm}^3$$

Problem 9. **Calculate the temperature at which 28 g of N_2 will occupy a volume of 10·0 litres at 2·46 atmosphere.** ***(M.L.N.R. Allahabad 1987)***

Solution. 28 g N_2 = 1 mole of N_2.

Applying $PV = n\,RT$,

$2{\cdot}46 \times 10 = 1 \times 0{\cdot}0821 \times T$. This gives

$$T = 299\cdot6 \text{ K}$$

Problem 10. **At 18°C and 765 torr, 1·299 L of a gas weighs 2·71 g. Calculate the approximate molecular weight of the gas.** ***(I.S.M. Dhanbad 1987)***

Solution. $P_1 = 765$ torr, $V_1 = 1{\cdot}299$ L, $T_1 = 291$ K

Converting to volume at NTP, $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$,

we get $$\frac{765 \times 1\cdot299}{291} = \frac{760 \times V_2}{273}$$

or $$V_2 = 1\cdot2267 \text{ L.}$$

$$\text{Mass of 22·4 L at STP} = \frac{2\cdot71}{1\cdot2267} \times 22\cdot4 \text{ g} = 49\cdot5 \text{ g}$$

∴ Molar mass = **49·5 g mol^{-1}**

Problem 11. **The volumes of ozone and chlorine diffusing during the same time are 35 ml and 29 ml respectively. If the molecular weight of chlorine is 71, calculate the molecular weight of ozone.** ***(B.I.T. Ranchi 1988)***

Solution. Applying Graham's law of diffusion,

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$$

or $$\frac{v_1/t}{v_2/t} = \sqrt{\frac{M_2}{M_1}} \quad \text{or} \quad \frac{v_1}{v_2} = \sqrt{\frac{M_2}{M_1}}$$

or $$\frac{v_{O_3}}{v_{Cl_2}} = \sqrt{\frac{M_{Cl_2}}{M_{O_3}}}$$

or $$\frac{35}{29} = \sqrt{\frac{71}{M_{O_3}}}$$

or $$M_{O_3} = 71 \times \left(\frac{29}{35}\right)^2 = \mathbf{48\cdot7}\ u.$$

Problem 12. **Which will diffuse faster, ammonia or CO_2 ? What are their relative rates of diffusion ?** ***(B.I.T. Ranchi 1989)***

Solution. $M_{NH_3} = 17$, $M_{CO_2} = 44$.

As rate $\propto \sqrt{\dfrac{1}{M}}$, hence NH_3 will diffuse faster

$$\frac{r_{NH_3}}{r_{CO_2}} = \sqrt{\frac{M_{CO_2}}{M_{NH_3}}} = \sqrt{\frac{44}{17}} = \mathbf{1\cdot609}$$

Problem 13. **An open vessel at 27°C is heated until $\frac{3}{5}$ parts of the air in it has been expelled. Assuming that the volume of the vessel remains constant, find the temperature to which the vessel has been heated.** ***(M.L.N.R. Allahabad 1990)***

Solution. As the vessel is open, pressure and volume remain constant. Thus if n_1 moles are present at T_1 and n_2 moles are present at T_2, we can write

$$PV = n_1 R\,T_1\ ;\ PV = n_2\,RT_2$$

Hence $n_1\,RT_1 = n_2\,RT_2$ or $n_1\,T_1 = n_2\,T_2$

or $$\frac{n_1}{n_2} = \frac{T_2}{T_1}$$

Suppose the no. of moles of air originally present $= n$

After heating, no. of moles of air expelled $= \frac{3}{5}\,n$

∴ No. of moles left after heating

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

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

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

or $$T_2 = \mathbf{750\ K}$$

Alternatively, suppose the volume of the vessel = V

i.e. Volume of air initially at 27°C = V

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

$\therefore$ Volume of air left at 27°C $= \frac{2}{5}$ V

However on heating to T°K, it would become = V

As pressure remains constant, (vessel being open),

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

Problem 14. **What is density of SO_2 gas at 27°C and 2 atmospheric pressure ? (At wts. S = 32, O = 16, R = 0·0821 L atm K^{-1} mol^{-1})** ***(C.E.E. Bihar 1997)***

Solution. $PV = nRT = \frac{w}{M} RT$

$$\Rightarrow d = \frac{w}{V} = \frac{PM}{RT} = \frac{2\ \text{atm} \times 64\ \text{g mol}^{-1}}{0{\cdot}0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$

$$= \mathbf{5{\cdot}1969\ g\ L^{-1}}$$

Problem 15. **Two flasks of equal volume connected by a narrow tube of negligible volume are filled with N_2 gas. When both are immersed in boiling water the gas pressure inside the system is 0·5 atm. Calculate the pressure of the system when one of the flasks is immersed in an ice-water mixture keeping the other in boiling order.** ***(C.E.E. Bihar 1998)***

Solution. Temp. of the gas when both the flasks are immersed in boiling water = 100°C = 373 K.

Pressure = 0·5 atm

Average temp. of the gas when one flask is immersed in ice and the other in boiling water

$$= \frac{0 + 100}{2} = 50°C = 323\ K$$

As volume remains constant, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{0{\cdot}5}{373} = \frac{P_2}{323}$$

or $P_2 = \frac{323}{373} \times 0{\cdot}5 = \mathbf{0{\cdot}433\ atm.}$

Problem 16. **What is the difference in pressure between the top and bottom of a vessel 76 cm deep at 27°C when filled with (*i*) water (*ii*) mercury ? Density of water at 27°C is 0·990 g cm^{-3} and that of mercury is 13·60 g cm^{-3}.** ***(C.E.E. Bihar 1998)***

Solution. Pressure = height × density × g

Case (i). Pressure

$= 76\ \text{cm} \times 0{\cdot}99\ \text{g / cm}^3 \times 981\ \text{cm / s}^2$

$= 7{\cdot}38 \times 10^4\ \text{dynes cm}^{-2}$

$= \mathbf{0{\cdot}073\ atm}$ (1 atm = $1{\cdot}013 \times 10^6$ dynes cm^{-2})

Case (ii) Pressure

$= 76\ \text{cm} \times 13{\cdot}6\ \text{g / cm}^3 \times 981\ \text{cm/s}^2$

$= 1{\cdot}013 \times 10^6\ \text{dynes cm}^{-2} = \mathbf{1\ atm.}$

Problem 17. **For 10 minutes each, at 27°C, from two identical holes, nitrogen and an unknown gas are leaked into a common vessel of 3 L capacity. The resulting pressure is 4·18 bar and the mixture contains 0·4 mole of nitrogen. What is the molar mass of the unknown gas ?** ***(N.C.E.R.T.)***

Solution.

(i) Calculation of total number of moles in the mixture

P = 4·18 bar, V = 3 L, T = 27°C = 300 K

$$PV = nRT \text{ or } n = \frac{PV}{RT} = \frac{4{\cdot}18 \times 3}{0{\cdot}083 \times 300} = 0{\cdot}50\ \text{mol}$$

(ii) Calculation of number of moles diffused in the same time

No. of moles of N_2 present in the mixture

= 0·4 mol

$\therefore$ No. of moles of unknown gas = 0·5—0·4

= 0·1 mol

Thus in the same time (10 minutes), 0·4 mol of N_2 and 0·1 mol of unknown gas diffuse out.

(iii) Calculation of molar mass. As volumes under similar conditions are directly proportional to their number of moles, applying Graham's law of diffusion

$$\frac{r_{N_2}}{r_X} = \sqrt{\frac{M_X}{M_{N_2}}} \text{ or } \frac{n_{N_2}}{n_X} = \sqrt{\frac{M_X}{M_{N_2}}}$$

$$\text{i.e. } \frac{0{\cdot}4}{0{\cdot}1} = \sqrt{\frac{M_X}{28}} \text{ or } \mathbf{M_X = 448\ g\ mol^{-1}}$$

Problem 18. **Calculate the root mean square speed (*rms*) of ozone kept in a closed vessel at 20°C and pressure of 82 cm of Hg.** ***(Bihar C.E.E. 2003)***

Solution. Volume occupied by 1 mole of O_3 at 20°C and 82 cm pressure can be calculated as follows :

$$\frac{76 \times 22400}{273} = \frac{82 \times V}{293}$$

or $V = 22282\ cm^3$

$P = 82 \times 13{\cdot}6 \times 981\ \text{dynes / cm}^2$

$$u = \sqrt{\frac{3\ PV}{M}}$$

$$= \sqrt{\frac{3 \times 82 \times 13{\cdot}6 \times 981 \times 22282}{48}}$$

$= \mathbf{3{\cdot}90 \times 10^4\ cm/sec.}$

I.I.T. (MAINS) SPECIAL

Problem 1. **Calculate the critical constants of a gas whose van der Waal's constants are : $a = 0\cdot751\ \text{L}^2\ \text{atm mol}^{-2}$ and $b = 0\cdot0226\ \text{L mol}^{-1}$.**

Solution. $P_c = \dfrac{a}{27\,b^2} = \dfrac{0\cdot751\ \text{L}^2\ \text{atm mol}^{-2}}{27 \times (0\cdot0226\ \text{L mol}^{-1})^2}$

$= \mathbf{54\cdot5\ atm}$

$$T_c = \frac{8\,a}{27\,R\,b}$$

$$= \frac{8 \times 0\cdot751\ \text{L}^2\ \text{atm mol}^{-2}}{27 \times 0\cdot0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 0\cdot0226\ \text{L mol}^{-1}}$$

$= \mathbf{120\ K}$

$V_c = 3\,b = 3 \times 0\cdot0226\ \text{L mol}^{-1}$

$= \mathbf{0\cdot0678\ L\ mol^{-1}}$.

Problem 2. **The critical constants of a gas are as follows :**

$P_c = 45\cdot6$ atm, $V_c = 0\cdot0987\ \text{L mol}^{-1}$ and

$T_c = 190\cdot6$ K.

Calculate the van der Waal's constants of the gas. Also calculate the radius of the gas molecule assuming it to be spherical.

Solution. $V_c = 3\,b$ gives $b = \dfrac{V_c}{3}$

$= \dfrac{0\cdot0987\ \text{L mol}^{-1}}{3} = \mathbf{0\cdot0329\ L\ mol^{-1}}$

$P_c = \dfrac{a}{27\,b^2}$ gives $a = 27\,P_c\,b^2$

$= 27\,P_c \left(\dfrac{V_c}{3}\right)^2 = 3\,P_c\,V_c^2$

i.e. $a = 3\,P_c\,V_c^2$

$= 3\,(45\cdot6\ \text{atm})\,(0\cdot0987\ \text{L mol}^{-1})^2$

$= \mathbf{1\cdot333\ L^2\ atm\ mol^{-2}}$

Calculation of radius of the gas molecule

Value of b per molecule

$= \dfrac{b}{N_A} = \dfrac{0\cdot0329 \times 10^3\ \text{cm}^3\ \text{mol}^{-1}}{6\cdot022 \times 10^{23}\ \text{mol}^{-1}}$

$= 5\cdot46 \times 10^{-23}\ \text{cm}^3$

But $b = 4\,v_m \quad \therefore\ v_m = \dfrac{b}{4} = \dfrac{5\cdot46 \times 10^{-23}}{4}\ \text{cm}^3$

$= 1\cdot365 \times 10^{-23}\ \text{cm}^3$

If r is the radius of the gas molecule, then

$\dfrac{4}{3}\pi r^3 = 1\cdot365 \times 10^{-23}\ \text{cm}^3$

or $r^3 = \dfrac{3}{4} \times \dfrac{7}{22} \times 1\cdot365 \times 10^{-23}\ \text{cm}^3$

$= 3\cdot257 \times 10^{-24}\ \text{cm}^3$

$r = (3\cdot257)^{1/3} \times 10^{-8}\ \text{cm} = 1\cdot483 \times 10^{-8}\ \text{cm}$

$= \mathbf{1\cdot483\ \text{Å}}$ or $\mathbf{148\cdot3\ pm}$

[Put $x = (3\cdot257)^{1/3}\ \therefore \log x = \dfrac{1}{3}\log 3\cdot257$

$= \dfrac{1}{3} \times 0\cdot5128 = 0\cdot1709$ or $x = 1\cdot483$]

Problem 3. **A mixture of CO and CO_2 is found to have a density of $1\cdot50\ g\ L^{-1}$ at 20°C and 740 mm pressure. Calculate the composition of the mixture.**

Solution. *Calculation of average molecular mass of the mixture*

$M = \dfrac{d\,RT}{P}$

$= \dfrac{1\cdot50\ g\ \text{L}^{-1} \times 0\cdot0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 293\ \text{K}}{(740/760)\ \text{atm}}$

$= 37\cdot06$

Calculation of percentage composition. Suppose mol % of CO in the mixture $= x$

Then mol% of CO_2 in the mixture $= (100 - x)$

Average molecular mass

$= \dfrac{x \times 28 + (100 - x) \times 44}{100}$

$\therefore \quad \dfrac{28x + 4400 - 44x}{100} = 37\cdot06$

or $\quad 16x = 4400 - 3706 = 694$

or $\quad x = 694/16 = 43\cdot38$

$\therefore$ **Mol % of CO = 43·38**

and Mol % of CO_2 = 100 − 43·38 = **56·62.**

Problem 4. **Assuming that dry air contains 79% N_2 and 21% O_2 by volume, calculate the density of dry air at 25°C and 1 atmospheric pressure. Also calculate the density of the moist air under the same conditions if it has a relative humidity of 40%. The vapour pressure of water at 25°C is 23·76 mm.**

Solution. **Calculation of density of dry air.** Density of air means the mass of air per litre.

First let us convert 1 L (1000 cm³) of air at 25°C, 1 atm pressure to the volume at S.T.P.

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

$$\therefore \quad \frac{1\text{ atm}\times 1000\text{ cm}^3}{298\text{ K}}=\frac{1\text{ atm}\times V_2}{273\text{ K}}$$

or $V_2 = 916\cdot 1\text{ cm}^3$

As air contains 79% N_2 and 21% O_2,

∴ Volume of N_2 at S.T.P. in the air

$$=\frac{79}{100}\times 916\cdot 1\text{ cm}^3 = 723\cdot 72\text{ cm}^3$$

Volume of O_2 at S.T.P. in the air

$$=\frac{21}{100}\times 916\cdot 1\text{ cm}^3 = 193\cdot 38\text{ cm}^3$$

Mass of $723\cdot 72\text{ cm}^3$ of N_2 at S.T.P.

$$=\frac{28}{22400}\times 723\cdot 72 = 0\cdot 905\,g$$

Mass of $193\cdot 38\text{ cm}^3$ of O_2 at S.T.P.

$$=\frac{32}{22400}\times 193\cdot 38 = 0\cdot 276\,g$$

∴ Total mass of 1 L of air at 25°C and 1 atm

$$= 0\cdot 905 + 0\cdot 276\,g = 1\cdot 181\,g$$

Hence density of dry air = **1·181 *g***

Calculation of density of moist air

% Relative humidity

$$=\frac{\textbf{Partial pressure of } H_2O \textbf{ vapours}}{\text{Vapour pressure of } H_2O \text{ at the same temp.}}\times 100$$

∴ Partial pressure of H_2O vapours

$$=\frac{40\times 23\cdot 76}{100} = 9\cdot 5\text{ mm}$$

As total pressure = 1 atm = 760 mm,

∴ Pressure of $N_2 + O_2$ in the air

$$= 760 - 9\cdot 5 = 750\cdot 5\text{ mm}$$

As N_2 and O_2 are present in the air in the ratio of 79 : 21 volume.

∴ Partial pressure of $N_2 = \frac{79}{100}\times 750\cdot 5\text{ mm} =$ 592·9 mm

and Partial pressure of $O_2 = 750\cdot 5 - 529\cdot 9 =$ 157·6 mm

Applying gas equation $PV = nRT$ *i.e.* $n=\frac{PV}{RT}$

No. of moles of H_2O in the air (n_{H_2O})

$$=\frac{(9\cdot 5/760)\text{ atm}\times 1\text{ L}}{0\cdot 0821\text{ L atm K}^{-1}\text{ mol}^{-1}\times 298\text{ K}}$$

$$= 5\cdot 1\times 10^{-4}$$

No. of moles of N_2 in the air (n_{N_2})

$$=\frac{(592\cdot 9/760)\times 1}{0\cdot 0821\times 298} = 3\cdot 19\times 10^{-2}$$

No. of moles of O_2 in the air (n_{O_2})

$$=\frac{(157\cdot 6/760)\times 1}{0\cdot 0821\times 298} = 8\cdot 48\times 10^{-3}$$

∴ Total mass of 1 L of air

$$= 5\cdot 1\times 10^{-4}\times 18 + 3\cdot 19\times 10^{-2}\times 28 + 8\cdot 48\times 10^{-3}\times 32$$

$$= 0\cdot 00918 + 0\cdot 8932 + 0\cdot 02714 = 1\cdot 174\,g$$

Hence density of moist air = **1·174 *g* L⁻¹**.

Note. Density of dry air can also be calculated by this method.

Problem 5. **At room temperature ammonia gas at 1 atm pressure and HCl gas at pressure P atm are allowed to effuse through identical pin holes from opposite ends of a glass tube of 1 meter length and of uniform area of cross-section. NH_4Cl is first formed at a distance of 60 cm from the end through which HCl gas was sent in. Calculate the value of P.** ***(I.I.T. 1982)***

Solution. According to Graham's law of diffusion for gases at different pressures,

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

$$\frac{60}{40}=\frac{P}{1}\sqrt{\frac{17}{36\cdot 5}}$$

or $$P=\left(\frac{60}{40}\right)\times\sqrt{\frac{36\cdot 5}{17}}$$

$$= 1\cdot 5\times 1\cdot 465 = \mathbf{2\cdot 198\text{ atm.}}$$

Problem 6. **A spherical balloon of 21 cm diameter is to be filled with hydrogen at NTP from a cylinder containing the gas at 20 atmosphere at 27°C. If the cylinder can hold 2·82 litres of water, calculate the number of balloons that can be filled up.** ***(I.I.T. 1987)***

Solution. Volume of the balloon

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

$$= 4851\text{ cm}^3$$

Volume of the cylinder = 2·82 litres = 2820 cm³

Pressure = 20 atm.,

Temperature = 300 K

Converting this to the volume at NTP

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

we get $$\frac{20\times 2820}{300}=\frac{1\times V_2}{273}$$

or $V_2 = 51324\text{ cm}^3$.

When the pressure in the cylinder is reduced to one atmosphere, no more H_2 will be released and hence 2820 cm^3 of H_2 will be left in it. Hence volume of H_2 used in filling the balloons

$$= 51324 - 2820\ cm^3 = 48504\ cm^3.$$

Number of balloons filled

$$= 48504/4851 = \mathbf{10}$$

Problem 7. **The average velocity at T°_1 K and the most probable velocity at T°_2 K of CO_2 gas is $9{\cdot}0 \times 10^4$ cm sec^{-1}. Calculate the values of T_1 and T_2.** ***(I.I.T. 1990)***

Solution. Average velocity $= 0{\cdot}9213 \times$ R.M.S. velocity

$$= 0{\cdot}9213 \times \sqrt{\frac{3\,RT}{M}}$$

$$\therefore\ 9 \times 10^4 = 0{\cdot}9213 \times \sqrt{\frac{3 \times 8{\cdot}3 \times 10^7 \times T_1}{44}}$$

This on solving gives

$$T_1 = \mathbf{1691\ K}$$

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

$$\therefore\quad 9 \times 10^4 = \sqrt{\frac{2 \times 8{\cdot}3 \times 10^7 \times T_2}{44}}$$

This on solving gives $T_2 = \mathbf{2147\ K}$

Problem 8. **At room temperature, the following reaction goes to completion**

$$\mathbf{2\,NO + O_2 \longrightarrow 2\,NO_2 \longrightarrow N_2O_4}$$

Dimer N_2O_4 at 268 K is solid. A 250 *m*L flask and a 100 *m*L flask are separated by a stop- cock. At 300 K, the nitric oxide in the larger flask exerts pressure of $1{\cdot}053$ atm and the smaller one contains O_2 at $0{\cdot}789$ atm. The gases are mixed by opening the stop-cock and after the end of the reaction, the flasks are cooled to 220 K. Neglecting the vapour pressure of dimer, find out the pressure and composition of the gas remaining at 220 K. Assume gases behave ideally. ***(I.I.T. 1992)***

Solution. For NO : $V = 250\ mL = 0{\cdot}25$ L,
$T = 300$ K, $P = 1{\cdot}053$ atm

$$\therefore\ n_{NO} = \frac{PV}{RT} = \frac{1{\cdot}053 \times 0{\cdot}25}{0{\cdot}0821 \times 300} = 1{\cdot}069 \times 10^{-2}$$

For O_2 : $V = 100\ mL = 0{\cdot}1$ L, $T = 300$ K,
$P = 0{\cdot}789$ atm

$$\therefore\quad n_{O_2} = \frac{0{\cdot}789 \times 0{\cdot}1}{0{\cdot}0821 \times 300} = 0{\cdot}32 \times 10^{-2}$$

Now

	$2\,NO$	$+\ O_2$	$\longrightarrow 2\,NO_2$
Moles before reaction	$1{\cdot}602 \times 10^{-2}$	$0{\cdot}32 \times 10^{-2}$	0
Moles after reaction	$1{\cdot}602 \times 10^{-2}$ $- 2 \times 0{\cdot}32 \times 10^{-2}$	0	$0{\cdot}32 \times 10^{-2}$

$$= 0{\cdot}429 \times 10^{-2}$$

Thus, moles of NO left $= 4{\cdot}29 \times 10^{-3}$

Now $T = 220$ K *(Given)*,

$$V = \frac{250 + 100}{1000}\ L = 0{\cdot}35\ L$$

Applying gas equation, $P_{NO}\,V = n\,RT$

$$P_{NO} = \frac{n\,RT}{V}$$

$$= \frac{(4{\cdot}29 \times 10^{-3}\ mol)\ (0{\cdot}0821\ L\ atm\ K^{-1}\ mol^{-1})\ (220\ K)}{0{\cdot}35\ L}$$

$$= \mathbf{0{\cdot}221\ atm.}$$

Problem 9. **A gas bulb of 1 litre capacity contains $2{\cdot}0 \times 10^{21}$ molecules of nitrogen exerting a pressure of $7{\cdot}57 \times 10^3$ N m^{-2}. Calculate the root mean square (r.m.s.) speed and the temperature of the gas molecules. If the ratio of the most probable speed to the root mean square speed is $0{\cdot}82$, calculate the most probable speed for these molecules at this temperature.** ***(I.I.T. 1993)***

Solution. Volume of gas = 1 litre $= 10^{-3}\ m^3$

Pressure $= 7{\cdot}57 \times 10^3\ Nm^{-2}$

No. of moles of the gas

$$= (2{\cdot}0 \times 10^{21}) / (6{\cdot}02 \times 10^{23}) = 0{\cdot}00332$$

Applying $PV = nRT$

$$(7{\cdot}57 \times 10^3) \times 10^{-3} = 0{\cdot}00332 \times 8{\cdot}314 \times T$$

or $T = \mathbf{274{\cdot}25\ K}$

$$\text{Root Mean Square speed} = \sqrt{\frac{3\,RT}{M}}$$

$$= \sqrt{\frac{3 \times 8{\cdot}314 \times 10^7 \times 274{\cdot}25}{28}}$$

$$= \mathbf{49426{\cdot}5\ cm\ s^{-1}}$$

$$\frac{\text{Most probable speed}}{\text{Root Mean Square speed}} = 0{\cdot}82\ \textit{(Given)}$$

$\therefore$ Most probable speed $= 0{\cdot}82 \times$ R. M. S. Speed

$$= 0{\cdot}82 \times 49426{\cdot}5 = \mathbf{40529{\cdot}7\ cm\ s^{-1}}$$

Problem 10. **A 4 : 1 molar mixture of He and CH_4 is contained in a vessel at 20 bar pressure. Due to a hole in the vessel the gas mixture leaks out. What is the composition of the mixture effusing out initially ?**

(I.I.T. 1994)

Solution. Applying Graham's law of effusion,

$$\frac{r_{He}}{r_{CH_4}} = \sqrt{\frac{M_{CH_4}}{M_{He}}} = \sqrt{\frac{16}{4}} = \sqrt{4} = 2$$

i.e. He diffuses two times faster than CH_4.

$\therefore$ Molar ratio of He : CH_4 effusing out initially

= 8 : 1

Problem 11. **An LPG (liquefied petroleum gas) cylinder weighs 14·8 kg when empty. When full, it weighs 29·0 kg and shows a pressure of 2·5 atm. In the course of use at 27°C, the weight of the full cylinder reduced to 23·2 kg. Find out the volume of the gas in cubic metres used up at the normal usage conditions, and the final pressure inside the cylinder. Assume LPG to be *n*-butane with normal boiling point of 0°C.**

(I.I.T. 1994)

Solution. Decrease in the amount of LPG

$$= 29{\cdot}0 - 23{\cdot}2 = 5{\cdot}8 \text{ kg}$$

$$= \frac{5800}{58} \text{ moles} = 100 \text{ moles}$$

Volume of 100 moles at 1 atm and 300 K

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

$$= \frac{100 \text{ moles} \times 0{\cdot}0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300\text{K}}{1 \text{ atm}}$$

$$= 2463\text{L} = 2463 \times 10^{-3} m = 2{\cdot}463 \text{ m}^3$$

Final pressure inside the cylinder. As the cylinder contains liquefied petroleum gas in equilibrium with its vapours, therefore so long as temperature remains constant and some LPG is present, pressure will remain constant. As the cylinder still contains LPG = 23·2 – 14·8 = 8·4 kg, pressure inside the cylinder will be same *i.e.* **2·5 atm.**

Problem 12. **A balloon of diameter 20 m weighs 100 kg. Calculate its pay-load if it is filled with He at 1·0 atm and 27°C. Density of the air is 1·2 kg cm^{-3}. (R = 0·082 dm^3 atm K^{-1} mol^{-1})** ***(Roorkee 1994)***

Solution. Radius of the balloon = 10 *m*

$\therefore$ Volume of the balloon $= \frac{4}{3}\pi r^3$

$$= \frac{4}{3} \times \frac{22}{7} \times (10)^3 \, m^3 = 4190{\cdot}5 \, m^3$$

Volume of He filled at 1 atm and 27°C = 4190·5 m^3

i.e. P = 1 atm, V = 4190·5 m^3, T = 300 K

R = 0·082 dm^3 atm K^{-1} mol^{-1} (Given)

PV = *n*RT

i.e. (1 atm) (4190·5 m^3)

$$= n \times (0{\cdot}082 \times 10^{-3} \, m^3 \text{ atm K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})$$

This gives $n = \dfrac{4190{\cdot}5}{0{\cdot}082 \times 10^{-3} \times 300}$

= 170345·5 moles

Weight of 170345·5 moles He

$$= 170345{\cdot}5 \times \frac{4}{1000} \text{ kg} = 681{\cdot}4 \text{ kg}$$

Total weight of the balloon filled with He

= 100 + 681·4 kg = 781·4 kg

Maximum weight of the air that can be displaced by balloon to go up = Volume × Density

= 4190·5 × 1·2 = 5028·6 kg

$\therefore$ Pay-load *i.e.* extra load that can be attached to the balloon = 5028·6 – 781·4 = 4247·2 kg

Problem 13. **The composition of the equilibrium mixture ($Cl_2 \rightleftharpoons 2Cl$), which is attained at 1200°C is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1·80 mm Hg pressure, the mixture effuses 1·16 times as fast as Krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (Atomic weight of Kr = 84)** ***(I.I.T. 1995)***

Solution. $\dfrac{r_{mix}}{r_{Kr}} = \sqrt{\dfrac{M_{Kr}}{M_{mix}}}$

i.e. $1{\cdot}16 = \sqrt{\dfrac{84}{M_{mix}}}$

or $M_{mix} = 62{\cdot}43$

If *x* moles of Cl_2 dissociate at equilibrium, then

$$\begin{array}{lcc} & Cl_2 \rightleftharpoons & 2Cl \\ \text{At. eqm.} & 1 - x & 2x \end{array}$$

Average molecular mass of the mixture

$$= \frac{(1 - x) \times 71 + 2x \times 35{\cdot}5}{(1 - x) + 2x} = \frac{71}{1 + x}$$

Hence $\dfrac{71}{1 + x} = 62{\cdot}43$ which gives $x = 0{\cdot}137$.

Hence fraction dissociated = **0·137**

Problem 14. **An iron cylinder contains helium at a pressure of 250 kPa at 300K. The cylinder can withstand a pressure of 1 × 10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. (M.P. of the cylinder = 1800 K)** ***(Roorkee 1995)***

Solution. $P_1 = 250$ K Pa, $\quad T_1 = 300$ K

$P_2 = ?$ $\quad T_2 = 1800$ K

Applying pressure — temperature law

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

$$\frac{250}{300} = \frac{P_2}{1800} \text{ or } P_2 = 1500 \text{ kPa}$$

As the cylinder can withstand a pressure of 10^6 Pa $= 10^3$ kPa $= 1000$ kPa, hence it will blow up.

Problem 15. **20 dm^3 of SO$_2$ diffuse through a porous partition in 60 *s*. What volume of O$_2$ will diffuse under similar conditions in 30*s* ?** ***(Roorkee 1996)***

Solution. $r_{SO_2} = \frac{20 \text{ dm}^3}{60\, s} = \frac{1}{3} \text{dm}^3 s^{-1}$

$$r_{O_2} = \frac{v\ dm^3}{30\, s} = \frac{v}{30} \text{dm}^3 \text{ s}^{-1}$$

Applying Graham's law of diffusion

$$\frac{r_{O_2}}{r_{SO_2}} = \sqrt{\frac{M_{SO_2}}{M_{O_2}}}$$

i.e. $\frac{v/30}{1/3} = \sqrt{\frac{64}{32}}$

or $\frac{v}{10} = \sqrt{2}$ $\quad$ or $\quad$ $v = 14 \cdot 14 \text{ dm}^3$

Problem 16. **Calculate the total pressure in a 10 L cylinder which contains 0·4g of helium, 1·6 g of oxygen and 1·4 g of nitrogen at 27°C. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour for gases. (R = 0·082 L atm K^{-1} mol^{-1}).** ***(Roorkee 1997)***

Solution. Total no. of moles of all the gases (n)

$$= \frac{0 \cdot 4}{4} + \frac{1 \cdot 6}{32} + \frac{1 \cdot 4}{28} = 0 \cdot 2$$

Volume of the gaseous mixture (V) = 10 L

Temp. (T) = 27 + 273 = 300 K,

$$R = 0 \cdot 082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

As gases have ideal behaviour,

$PV = nRT$

$$\text{or } P = \frac{nRT}{V} = \frac{0 \cdot 2 \times 0 \cdot 082 \times 300}{10} = 0 \cdot 492 \text{ atm}$$

$\therefore$ Partial pressure of helium

$$= \frac{0 \cdot 4/4}{0 \cdot 2} \times 0 \cdot 492 = \mathbf{0 \cdot 246 \text{ atm}}$$

Problem 17. **An evacuated glass vessel weighs 50·0 g when empty, 148·0 g when filled with a liquid of density 0·98 g ml^{-1} and 50·5 g when filled with an ideal gas at 760 mm Hg at 300 K. Determine the molecular weight of the gas.** ***(I.I.T. 1998)***

Solution. Volume of the liquid

$$= \frac{(148 - 50)\, g}{0 \cdot 98\ g \text{ mol}^{-1}} = 100 \text{ ml}$$

$$= 0 \cdot 1 \text{ litre}$$

This is the volume of the vessel and hence the volume of the gas.

For ideal gas, $PV = n\,RT = \frac{w}{M} RT$ or $M = \frac{wRT}{PV}$

$$= \frac{0 \cdot 5 \text{ g} \times 0 \cdot 082 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{1 \text{ atm} \times 0 \cdot 1 \text{ L}}$$

$$= \mathbf{123\ g\ mol^{-1}}$$

Problem 18. **Using van der Waals equation calculate the constant '*a*' when two moles of a gas confined in a four litre flask exerts a pressure of 11·0 atmosphere at a temperature of 300 K. The value of '*b*' is 0·05 lit mol^{-1}** ***(I.I.T. 1998)***

Solution. $\left(P + \frac{a\,n^2}{V^2}\right)(V - nb) = n\,RT$

$$\text{or} \quad a = \left(\frac{nRT}{V - nb} - P\right)\frac{V^2}{n^2}$$

$$= \left(\frac{2 \text{ mol} \times 0 \cdot 08205 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{4 \text{ L} - 2 \text{ mol} \times 0 \cdot 05 \text{ L mol}^{-1}} - 11 \text{ atm}\right) \frac{(4 \text{ L})^2}{(2 \text{ mol})^2}$$

$$= \mathbf{6 \cdot 49 \text{ atm L}^2 \text{ mol}^{-2}}$$

Problem 19. **A glass bulb contains 2·24 L of H$_2$ and 1·12 L of D$_2$ at S.T.P. It is connected to a fully evacuated bulb by a stopcock with a small opening. The stopcock is opened for sometime and then closed. The first bulb now contains 0·10 g of D$_2$. Calculate the percentage composition by weight of the gases in the second bulb.** ***(Roorkee 1998)***

Solution. Weight of 2·24 L of H$_2$ at S.T.P. = 0·2 g

= 0·1 mol (Mol. mass of H$_2$ = 2)

Weight of 1·12 L of D$_2$ at S.T.P. = 0·2 g

= 0·05 mol (Mol mass of D$_2$ = 4)

As number of moles of the two gases are different but V and T are same, therefore, their partial pressures will be different *i.e.* in the ratio of their number of moles. Thus

$$\frac{P_{H_2}}{P_{D_2}} = \frac{n_{H_2}}{n_{D_2}} = \frac{0 \cdot 1}{0 \cdot 05} = 2$$

Now D$_2$ present in the first bulb = 0·1 g (*Given*)

$\therefore$ D$_2$ diffused into the second bulb

= 0·2 — 0·1 = 0·1 g = 0·56 L at S.T.P.

$$\text{Now} \quad \frac{r_{H_2}}{r_{D_2}} = \frac{P_{H_2}}{P_{D_2}} \times \sqrt{\frac{M_{D_2}}{M_{H_2}}}$$

or $\frac{v_{H_2}}{t} \times \frac{t}{v_{D_2}} = \frac{P_{H_2}}{P_{D_2}} \times \sqrt{\frac{M_{D_2}}{M_{H_2}}}$

$$\frac{v_{H_2}}{t} \times \frac{t}{0 \cdot 56 \text{ L}} = 2 \times \sqrt{\frac{4}{2}}$$

or $v_{H_2} = 1 \cdot 584 \text{ L} = 0 \cdot 14 \, g$ of H_2

∴ Weight of the gases in 2nd bulb

$$= 0 \cdot 10 \, g \, (D_2) + 0 \cdot 14 \, g \, (H_2) = 0 \cdot 24 \, g$$

Hence in the 2nd bulb,

% of D_2 by weight $= \frac{0 \cdot 10}{0 \cdot 24} \times 100 = \mathbf{41 \cdot 67\%}$

% of H_2 by weight $= 100 - 41 \cdot 67 = \mathbf{58 \cdot 33\%}$.

Problem 20. **If the volume occupied by CO_2 molecules is negligible, then calculate the pressure exerted by one mole of CO_2 gas at 273 K ($a = 3 \cdot 592$ atm litre^{-2} mol^{-2})** **(*I.I.T. 2000*)**

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

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

or $P = \frac{RT}{V} - \frac{a}{V^2}$

or $PV^2 - RTV + a = 0$

This equation is quadratic in V. Hence

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

As V can have only one value at P and T, hence we must have $R^2 T^2 - 4aP = 0$

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

$$= \frac{(0 \cdot 0821 \text{ L atm K}^{-1} \text{ mol}^{-1})^2 (273 \text{ K})^2}{4 \times 3 \cdot 592 \text{ atm L}^{-2} \text{ mol}^{-2}}$$

$$= \mathbf{34 \cdot 96 \text{ atm}}$$

Problem 21. **One mole of nitrogen gas at 0·8 atm takes 38 *s* to diffuse through a pin hole whereas one mole of an unknown compound of Xenon with fluorine at 1·6 atm takes 57 *s* to diffuse through the same hole. Calculate the molecular formula of the compound.** **(*I.I.T. 1999*)**

Solution. Rate of diffusion $\propto \frac{P}{\sqrt{M}}$

$$\therefore \quad \frac{r_{N_2}}{r_X} = \frac{P_{N_2}}{P_X} \times \sqrt{\frac{M_X}{M_{N_2}}}$$

But $r_{N_2} = 1/38 \text{ mol } s^{-1}$ and $r_X = 1/57 \text{ mol } s^{-1}$

$$\therefore \quad \frac{r_{N_2}}{r_X} = \frac{1/38}{1/57} = \frac{57}{38} = \frac{3}{2} = \frac{0 \cdot 8}{1 \cdot 6} \sqrt{\frac{M_X}{28}}$$

or $\sqrt{M_X} = 3 \times \sqrt{28}$ or $M_X = 9 \times 28 = 252$

Atomic mass of Xe = 131 *u*

∴ Mass of F atoms = 252 – 131 = 121 *u*

Atomic mass of F = 19 *u*

∴ No. of F-atoms $= \frac{121}{19} \approx 6$

Hence the compound is **XeF_6**.

Problem 22. **The pressure exerted by 12 *g* of an ideal gas at temperature *t*°C in a vessel of volume V litre is one atm. When the temperature is increased by 10 degrees at the same volume, the pressure increases by 10%. Calculate the temperature *t* and volume V (Molecular weight of the gas = 120).** **(*I.I.T. 1999*)**

Solution. Applying PV = *n*RT

In the 1st case,

$$1 \times V = \frac{12}{120} \times R \times (273 + t) \qquad ...(i)$$

In the 2nd case,

$$1 \cdot 1 \times V = \frac{12}{120} \times R \times (283 + t) \qquad ...(ii)$$

Dividing (*i*) by (*ii*), $1/1 \cdot 1 = (273 + t)/(283 + t)$. On solving it gives $t = -173$°C. Putting in (*i*) $V = 0 \cdot 1 \times 0 \cdot 082 \times 100 = \mathbf{0 \cdot 82}$ **litre.**

Problem 23. **The compression factor (compressibility factor) for one mole of a van der Waals gas at 0°C and 100 atm pressure is found to be 0·5. Assuming that the volume of a gas molecule is negligible, calculate the van der Waals constant *a*.** **(*I.I.T. 2001*)**

Solution. $Z = \frac{PV}{nRT}$ *i.e.* $0 \cdot 5 = \frac{100 \times V}{1 \times 0 \cdot 082 \times 273}$

or $V = 0 \cdot 1119$ L

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

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

or $PV + \frac{a}{V} = RT$ or $\frac{PV}{RT} + \frac{a}{VRT} = 1$

or $a = \left(1 - \frac{PV}{RT}\right) VRT$

$$= (1 - 0 \cdot 5) \, 0 \cdot 1119 \times 0 \cdot 082 \times 273$$

$$= \mathbf{1 \cdot 252 \text{ atm L}^2 \text{ mol}^{-2}}$$

Problem 24. **Pay load is defined as the difference between the mass of the displaced air and the mass of the balloon. Calculate the pay load when a balloon of radius 10 m, mass 100 kg is filled with helium at 1·66 bar at 27°C (Density of air = 1·2 kg m^{-3} and R = 0·0833 bar dm^3 K^{-1} mol^{-1})** (*N.C.E.R.T.*)

Solution. Proceed as in solved example 12, page 2/65. **[Ans. 3811·1 kg]**

Problem 25. **The density of the vapour of a substance at 1 atm pressure and 500 K is 0·36 kg m^{-3}. The vapour effuses through a small hole at a rate of 1·33 times faster than oxygen under the same condition.**

(*a*) Determine (*i*) molecular weight (*ii*) molar volume (*iii*) compression factor (Z) of the vapour and (*iv*) which forces among the gas molecules are dominating, the attractive or the repulsive ?

(*b*) If the vapour behaves ideally at 1000 K, determine the average translational kinetic energy of the molecule. ***(I.I.T. 2002)***

Solution. (*a*) (*i*) $d = 0 \cdot 36 \text{ kg m}^{-3}$. By Graham's law of diffusion,

$$\frac{r_v}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_v}}$$

i.e. $$1 \cdot 33 = \sqrt{\frac{32}{M_v}} \quad \text{or} \quad M_v = \mathbf{18 \cdot 09}$$

(*ii*) $0 \cdot 36 \text{ kg m}^{-3} = 0 \cdot 36 \text{ g L}^{-1}$

i.e. 0·36 *g* of vapour have volume = 1 L

∴ 1 mol *i.e.* 18·09 *g* of vapour will have volume

$$= \frac{1}{0 \cdot 36} \times 18 \cdot 09 = \mathbf{50 \cdot 25 \ L}$$

(*iii*) Compressibility factor (Z) = $\frac{PV}{RT}$

$$= \frac{1 \text{ atm} \times 50 \cdot 25 \text{ L}}{0 \cdot 0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}$$

$$= \mathbf{1 \cdot 224}$$

(*iv*) As Z > 1, repulsive forces would dominate.

(*b*) $\overline{E} = \frac{3}{2} kT$

$$= \frac{3}{2} \times 1 \cdot 38 \times 10^{-23} \text{ JK}^{-1} \text{ molecule}^{-1} \times 1000 \text{ K}$$

$$= \mathbf{2 \cdot 07 \times 10^{-20} \text{ J per molecule}}$$

Problem 26. **The average velocity of gas molecules is 400 *m*/sec. Calculate its *rms* velocity at the same temperature.** ***(I.I.T. 2003)***

Solution. Average speed, $v = \sqrt{\frac{8 RT}{\pi M}}$.

Root mean square speed, $u = \sqrt{\frac{3 RT}{M}}$

$$\therefore \quad \frac{u}{v} = \sqrt{\frac{3 RT}{M} \times \frac{\pi M}{8 RT}}$$

$$= \sqrt{\frac{3\pi}{8}} = \sqrt{\frac{3 \times 3 \cdot 143}{8}} = 1 \cdot 085$$

$$\therefore \quad u = 1 \cdot 085 \times v = 1 \cdot 085 \times 400 \, ms^{-1}$$

$$= \mathbf{434 \ ms^{-1}}$$

or *directly*, $v = 0 \cdot 921 \, u$ *i.e.* $u = 1 \cdot 085 \times v$

MULTIPLE CHOICE QUESTIONS

For CBSE– PMT (Preliminary), IIT Screening, AIEEE, AIIMS, AFMC, DPMT, CPMT, BHU and All Other Competitive Examinations

1. The temperature at which the volume of the gas is zero is

(*a*) 0°C (*b*) 0°K

(*c*) 0°F (*d*) none of these.

2. With increase of temperature, the surface tension of a liquid

(*a*) increases (*b*) decreases

(*c*) remains unaffected

(*d*) may increase or decrease

3. Under identical experimental conditions, which one of the following pairs of gases will be most easy to separate by diffusion process ?

(*a*) O_2, N_2 (*b*) O_2, F_2

(*c*) H_2, D_2 (*d*) $^{235}U_6$, $^{238}UF_6$

4. Amorphous solids

(*a*) possess short range as well as long range order

(*b*) possess sharp melting points

(*c*) are isotropic

(*d*) undergo a clean cleavage when cut with knife.

5. A bottle of dry ammonia and a bottle of dry hydrogen chloride connected through a long tube are opened simultaneously at both ends, the white ammonium chloride ring first formed will be

(*a*) at the centre of the tube

(*b*) near the hydrogen chloride bottle

(*c*) near the ammonia bottle

(*d*) throughout the length of the tube.

(I.I.T. 1988)

ANSWERS

1. *b* **2.** *b* **3.** *c* **4.** *c* **5.** *b*

6. The rate of diffusion of methane at a given temperature is twice that of X. The molecular weight of X is

[✓ (*a*) 64·0] (*b*) 32·0
(*c*) 40·0 (*d*) 80·0.

(I.I.T. 1990, M.L.N.R. Allahabad 1995, Kerala E.E.E. 2001)

7. The density of neon will be highest at

(*a*) STP [✓ (*b*) 0°C, 2 atm]
(*c*) 273°C, 1 atm (*d*) 273°C, 2 atm.

(I.I.T. 1990)

8. According to kinetic theory of gases, for a diatomic molecule

(*a*) The pressure exerted by the gas is proportional to the mean velocity of the molecule
(*b*) The pressure exerted by the gas is proportional to the root mean square velocity of the molecule
(*c*) The root mean square velocity of the molecule is inversely proportional to temperature
[✓ (*d*) The mean translational kinetic energy of the molecule is proportional to the absolute temperature.]

(I.I.T. 1991)

9. At the same temperature and pressure, which of the following gases will have the highest kinetic energy per mole ?

(*a*) H_2 (*b*) O_2
(*c*) CH_4
[✓ (*d*) All will have equal value.]

(M.L.N.R. Allahabad 1991)

10. At constant volume, for a fixed number of moles of a gas, the pressure of the gas increases with rise of temperature due to

[✓ (*a*) Increase in average molecular speed]
(*b*) increased rate of collisions amongst molecules
(*c*) increase in molecular attraction
(*d*) decrease in mean free path. *(I.I.T. 1992)*

11. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is

(*a*) 1 : 2 (*b*) 1 : 1
(*c*) 1 : 16 [✓ (*d*) 15 : 16.] *(I.I.T. 1993)*

12. At constant volume and temperature conditions, the rates of diffusion D_A and D_B of gases A and B having densities ρ_A and ρ_B are related by the expression

(*a*) $D_A = [D_B \cdot \rho_A/\rho_B]^{1/2}$
(*b*) $D_A = [D_B \cdot \rho_B/\rho_A]^{1/2}$
[✓ (*c*) $D_A = D_B\,(\rho_A/\rho_B)^{1/2}$]
[✓ (*d*) $D_A = D_B\,(\rho_B/\rho_A)^{1/2}$.] *(I.I.T. 1993)*

13. A gas behaves most like an ideal gas under conditions of

(*a*) High pressure and low temperature
(*b*) High temperature and high pressure
[✓ (*c*) Low pressure and high temperature]
(*d*) Low pressure and low temperature.

(I.I.T. 1993, 1999)

14. If vapour density of O_2 and H_2 are 16 and 1, then the ratio of rate of diffusion of H_2 to that of diffusion of O_2 is

(*a*) 16 (*b*) 1/16
[✓ (*c*) 4] (*d*) 1/4. *(C.P.M.T. 1993)*

15. Containers A, B and C of equal volume contain oxygen, neon and methane respectively at the same temperature and pressure. The correct increasing order of their masses is

(*a*) A < B < C (*b*) B < C < A
(*c*) C < A < B [✓ (*d*) C < B < A.]

(I.S.M. Dhanbad, 1994)

16. Temperature below which the gas does not obey ideal gas laws is

(*a*) Critical temperature
(*b*) Inversion temperature
[✓ (*c*) Boyle temperature] (*d*) Reduced temperature.

(Haryana C.E.E.T. 1994)

17. The volume of 0·0168 mol of O_2 obtained by decomposition of $KClO_3$ 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.

(U.P. C.E.E. 1996)

18. The vapour pressure of water at 300 K in a closed container is 0·4 atm. If the volume of the container is doubled, its vapour pressure at 300 K will be

(*a*) 0·8 atm (*b*) 0·2 atm
[✓ (*c*) 0·4 atm] (*d*) 0·6 atm.

(Haryana C.E.E.T. 1996)

ANSWERS

6. *a* 7. *b* 8. *d* 9. *d* 10. *a* 11. *d* 12. *d* 13. *c* 14. *c* 15. *d*
16. *c* 17. *d* 18. *c*

19. The ratio between the root mean square velocity of H_2 at 50 K and that of O_2 at 800 K is

(*a*) 4 (*b*) 2

(*c*) 1 (*d*) 1/4. *(I.I.T. 1996)*

20. X ml of H_2 gas effuses through a hole in a container in 5 seconds. The time taken for the effusion of the same volume of the gas specified below under identical conditions is

(*a*) 10 seconds : He (*b*) 20 seconds : O_2

(*c*) 25 seconds : CO (*d*) 55 seconds : CO_2.

(I.I.T. 1996)

21. The compressibility factor for an ideal gas is

(*a*) 1·5 (*b*) 1·0

(*c*) 2·0 (*d*) ∞. *(I.I.T. 1997)*

22. The critical temperature of water is higher than that of O_2 because the H_2O molecule has

(*a*) fewer electrons than O_2

(*b*) two covalent bonds (*c*) V-shape

(*d*) dipole moment. *(I.I.T. 1997)*

23. According to Graham's law at a given temperature, the ratio of the rates of diffusion r_A/r_B of gases A and B is given by

(*a*) $(P_A/P_B)(M_A/M_B)^{1/2}$

(*b*) $(M_A/M_B)(P_A/P_B)^{1/2}$

(*c*) $(P_A/P_B)(M_B/M_A)^{1/2}$

(*d*) $(M_A/M_B)(P_B/P_A)^{1/2}$.

(where P and M are the pressures and molecular weights of gases A and B respectively) *(I.I.T. 1998)*

24. Which one of the following statements is *wrong* for gases ?

(*a*) Gases do not have a definite shape and volume

(*b*) Volume of the gas is equal to the volume of the container confining the gas

(*c*) Confined gas exerts uniform pressure on the walls of its container in all directions

(*d*) Mass of the gas cannot be determined by weighing a container in which it is enclosed.

(C.B.S.E. P.M.T. 1999)

25. Which of the following expressions correctly represents the relationship between the average molar kinetic energy, KE, of CO and N_2 molecules at the same temperature ?

(*a*) $KE_{CO} = KE_{N_2}$

(*b*) $KE_{CO} > KE_{N_2}$

(*c*) $KE_{CO} < KE_{N_2}$

(*d*) cannot be predicted unless the volumes of the gases are given. *(C.B.S.E. P.M.T. 2000)*

26. Density ratio of O_2 and H_2 is 16 : 1. The ratio of their r.m.s. velocities will be

(*a*) 4 : 1 (*b*) 1 : 16

(*c*) 1 : 4 (*d*) 16 : 1.

(A.I.I.M.S. 2000)

27. Pressure of a mixture of 4 *g* of O_2 and 2 *g* of H_2 confined in a bulb of 1 litre at 0°C is

(*a*) 25·215 atm (*b*) 31·205 atm

(*c*) 45·215 atm (*d*) 15·210 atm.

(A.I.I.M.S. 2000)

28. Which of the following exhibits the weakest intermolecular forces ?

(*a*) NH_3 (*b*) HCl

(*c*) He (*d*) H_2O.

(A.I.I.M.S. 2000)

29. If 300 ml of a gas at 27°C is cooled to 7°C at constant pressure, its final volume will be

(*a*) 135 ml (*b*) 540 ml

(*c*) 350 ml (*d*) 280 ml.

(A.I.I.M.S. 2000)

30. At 0°C and one atm pressure, a gas occupies 100 cc. If the pressure is increased to one and a half-time and temperature is increased by one-third of absolute temperature, then final volume of the gas will be

(*a*) 80 cc (*b*) 88·9 cc

(*c*) 66·7 cc (*d*) 100 cc.

(D.C.E.E.E. 2000)

31. 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.

(D.C.E.E.E. 2000)

32. The relationship which describes the variation of vapour pressure with temperature is called

(*a*) Hess's law (*b*) Arrhenius equation

(*c*) Kirchoff's law

(*d*) Clausius-Clapeyron equation. *(B.H.U. 2000)*

ANSWERS

19. *c*	**20.** *b*	**21.** *b*	**22.** *d*	**23.** *c*	**24.** *d*	**25.** *a*	**26.** *c*	**27.** *a*	**28.** *c*
29. *d*	**30.** *b*	**31.** *d*	**32.** *d*						

33. 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. (*B.H.U. 2000*)

34. Gas equation PV = *n* RT is obeyed by

(*a*) only isothermal process

(*b*) only adiabatic process

[✓ (*c*) Both (*a*) and (*b*)]

(*d*) None of these. (*B.H.U. 2000*)

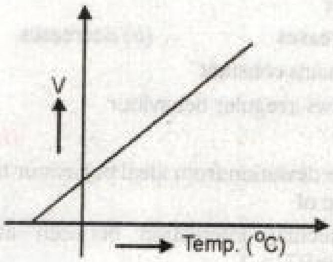
35. The rate of diffusion of a gas having molecular weight just double of nitrogen gas is 56 ml s^{-1}. The rate of diffusion of nitrogen will be

(*a*) 79·19 ml s^{-1} (*b*) 112·0 ml s^{-1}

(*c*) 56 ml s^{-1} (*d*) 90·0 ml s^{-1}.

(*C.P.M.T. 2000*)

36. The following graph illustrates



(*a*) Dalton's law [✓ (*b*) Charles 'law]

(*c*) Boyle's law (*d*) Gay-Lussac's law.

(*J.I.P.M.E.R. 2000*)

37. 4·4 *g* of a gas at STP occupies a volume of 2·24 L, the gas can be

(*a*) O_2 (*b*) CO

(*c*) NO_2 (*d*) CO_2.

(*Haryana C.E.E.T. 2000*)

38. The r.m.s. velocity of hydrogen is $\sqrt{7}$ times the r.m.s. velocity of nitrogen. If T is the temperature of the gas,

(*a*) $T(H_2) = T(N_2)$ (*b*) $T(H_2) > T(N_2)$

(*c*) $T(H_2) < T(N_2)$ (*d*) $T(H_2) = \sqrt{7}\,T(N_2)$.

(*I.I.T. 2000*)

39. The compressibility of a gas is less than unity at STP. Therefore

(*a*) $V_m > 22{\cdot}4$ litres (*b*) $V_m < 22{\cdot}4$ litres

(*c*) $V_m = 22{\cdot}4$ litres (*d*) $V_m = 44{\cdot}8$ litres.

(*I.I.T. 2000*)

40. At 100°C and 1 atm, if the density of liquid water is $1{\cdot}0\ g\ cm^{-3}$ and that of water vapour is $0{\cdot}0006\ g\ cm^{-3}$, then the volume occupied by water molecules in 1 litre of steam at that temperature is

(*a*) 6 cm^3 (*b*) 60 cm^3

(*c*) 0·6 cm^3 (*d*) 0·06 cm^3.

(*I.I.T. 2000*)

41. The root mean square velocity of an ideal gas at constant pressure varies with density (*d*) as

(*a*) d^2 (*b*) d

(*c*) $\sqrt{d}$ (*d*) $1/\sqrt{d}$.

(*I.I.T. 2001*)

42. At what temperature will the RMS of SO_2 be the same as that of O_2 at 303 K ?

(*a*) 273 K (*b*) 606 K

(*c*) 303 K (*d*) 403 K

(*K.C.E.T. 2001*)

43. The *r.m.s.* velocity of CO_2 at a temperature T (in kelvin) is *x* cm s^{-1}. At what temperature (in kelvin) the *r.m.s.* velocity of nitrous oxide would be 4 *x* cm s^{-1} ?

(*a*) 16 T (*b*) 2 T

(*c*) 4 T (*d*) 32 T

(*E.A.M.C.E.T. 2001*)

44. If the four tubes of a car are filled to the same pressure with N_2, O_2, H_2 and Ne separately, then which one will be filled first ?

(*a*) N_2 (*b*) O_2 (*c*) H_2 (*d*) Ne

(*Manipal P.M.T. 2002*)

45. Air at sea level is dense. This is practical application of

[✓ (*a*) Boyle's law]

(*b*) Charles' law

(*c*) Avogadro's law

(*d*) Dalton's law

[✓ (*e*) Gay-Lussac's law] (*Kerala C.E.E.T 2002*)

46. Which of the following has maximum root mean square velocity at the same temperature ?

(*a*) SO_2 (*b*) CO_2

ANSWERS

33. *a* 34. *c* 35. *a* 36. *b* 37. *d* 38. *c* 39. *b* 40. *c* 41. *d* 42. *b*
43. *a* 44. *c* 45. *a*

(*c*) O_2 (*d*) H_2

(Manipal P.M.T. 2002)

47. Kinetic theory of gases presumes the collisions between the molecules to be perfectly elastic because

(*a*) the molecules are rigid

(*b*) the temperature remains constant irrespective of collisions

(*c*) collisions will not split the molecules

(*d*) the molecules are tiny. *(K.C.E.T. 2002)*

48. The van der Waal's equation reduces itself to the ideal gas equation at

(*a*) high pressure and low temperature

(*b*) low pressure and low temperature

(*c*) low pressure and high temperature

(*d*) high pressure and high temperature.

(C.B.S.E. P.M.T. 2002)

49. For an ideal gas, number of moles per litre in terms of its pressure P, gas constant R and temperature T is

(*a*) PT/R (*b*) PRT

(*c*) P/RT (*d*) RT/P

(A.I.E.E.E. 2002)

50. Among the solids, the higher melting point is exhibited by

(*a*) Covalent solids

(*b*) Ionic solids

(*c*) Pseudo solids

(*d*) Molecular solids

(*e*) Amorphous solids *(Kerala M.E.E. 2002)*

51. When the temperature is raised, the viscosity of the liquid decreases. This is because

(*a*) Volume of the solution decreases

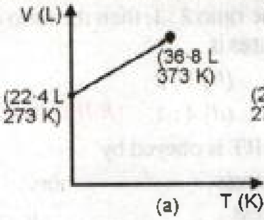
(*b*) increase in temperature increases the average kinetic energy of the molecules which overcomes the attractive force between them

(*c*) covalent and hydrogen bond forces decrease

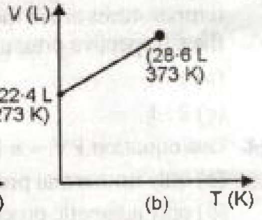
(*d*) attraction between the molecules increases

(*e*) none of the above *(Kerala M.E.E. 2002)*

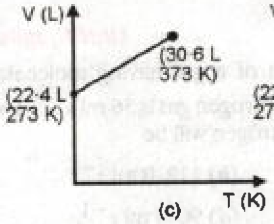
52. Which of the following volume (V)—temperature (T) plots represents the behaviour of one mole of an ideal gas at one atmospheric pressure ?



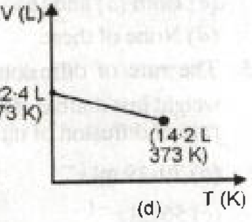
(a)



(b)



(c)



(d)

(I.I.T. Screening 2002)

53. When the temperature is increased, surface tension of water

(*a*) increases (*b*) decreases

(*c*) remains constant

(*d*) shows irregular behaviour

(I.I.T. 2002)

54. Positive deviation from ideal behaviour takes place because of

(*a*) molecular interaction between atoms and PV/*n*RT > 1

(*b*) molecular interaction between atoms and PV/*n*RT < 1

(*c*) finite size of the atoms and PV/*n*RT > 1

(*d*) finite size of the atoms and PV/*n*RT < 1

(I.I.T. 2003)

55. 0·5 mole of each of H_2, SO_2 and CH_4 are kept in a container. A hole was made in the container. After 3 hours, the order of partial pressures in the container will be

(*a*) $p_{SO_2} > p_{CH_4} > p_{H_2}$ (*b*) $p_{H_2} > p_{SO_2} > p_{CH_4}$

(*c*) $p_{CH_4} > p_{SO_2} > p_{H_2}$ (*d*) $p_{H_2} > p_{CH_4} > p_{SO_2}$

(D.P.M.T. 2003)

56. If *r.m.s* speed of gaseous molecules is *x* cm/sec at a pressure of *p* atm, then *r.m.s* at a pressure of 2*p* atm and constant temperature will be

(*a*) *x* (*b*) 2*x*

(*c*) 4*x* (*d*) *x*/4

(Orissa J.E.E. 2003)

ANSWERS

46. *d* **47.** *d* **48.** *c* **49.** *c* **50.** *a* **51.** *b* **52.** *c* **53.** *b* **54.** *a* **55.** *a*
56. *a*

57. In the equation PV = RT, the value of R will not depend on (one or more)

(*a*) the nature of the gas

(*b*) the temperature of the gas

(*c*) the pressure of the gas

(*d*) units of measurement.

58. Boyle's law may be expressed as (one or more)

(*a*) $(dP/dV)_T = K/V$ (*b*) $(dP/dV)_T = -K/V^2$

(*c*) $(dP/dV)_T = -K/V$

(*d*) $V \propto \frac{1}{P}$.

59. According to Charles' law (one or more)

(*a*) $(dV/dT)_P = K$ (*b*) $(dV/dT)_P = -K$

(*c*) $(dV/dT)_P = -K/T$ (*d*) $V \propto T$.

60. The root mean square velocity of one mole of a monoatomic gas having molar mass M is $U_{r.m.s.}$. The relation between the average kinetic energy (E) of the gas and U_{rms} is

(*a*) $U_{r.m.s.} = \sqrt{\frac{3E}{2M}}$

(*b*) $U_{r.m.s.} = \sqrt{\frac{2E}{3M}}$

(*c*) $U_{r.m.s.} = \sqrt{\frac{2E}{M}}$

(*d*) $U_{r.m.s.} = \sqrt{\frac{E}{3M}}$ (*I.I.T. 2004*)

61. As the temperature is raised from 20°C to 40°C, the average kinetic energy of neon atoms changes by a factor of which of the following ?

(*a*) 1/2 (*b*) $\sqrt{313/293}$

(*c*) 313/293 (*d*) 2 (*A.I.E.E.E. 2004*)

62. In van der Waals equation of state of the gas law, the constant *b* is a measure of

(*a*) intermolecular repulsions

(*b*) intermolecular attraction

(*c*) volume occupied by the molecules

(*d*) intermolecular collisions per unit volume

(*A.I.E.E.E. 2004*)

63. Containers A and B have same gas. Pressure, volume and temperature of A are all twice that of B. Then the ratio of the number of molecules of A and B are

(*a*) 1 : 2 (*b*) 2 : 1

(*c*) 1 : 4 (*d*) 4 : 1 (*A.F.M.C. 2004*)

64. The pressure and temperature of 4 dm^3 of carbon dioxide gas are doubled. Then the volume of carbon dioxide gas would be

(*a*) 2 dm^3 (*b*) 3 dm^3

(*c*) 4 dm^3 (*d*) 8 dm^3

(*Karnataka C.E.T. 2004*)

65. Hydrogen diffuses six times faster than gas A. The molar mass of gas A is

(*a*) 72 (*b*) 6

(*c*) 24 (*d*) 36

(*Karnataka C.E.T. 2004*)

66. What is the pressure of 2 mole of NH_3 at 27°C when its volume is 5 litre in van der Waals equation ? ($a = 4\cdot17, b = 0\cdot03711$)

(*a*) 10·33 atm (*b*) 9·33 atm

(*c*) 9·74 atm (*d*) 9·2 atm

(*Orissa J.E.E. 2004*)

67. The ratio of most probable velocity to the average velocity is

(*a*) $\pi/2$ (*b*) $2/\pi$

(*c*) $\sqrt{\pi}/2$ (*d*) $2/\sqrt{\pi}$

(*Orissa J.E.E. 2004*)

68. What is the kinetic energy of 1 *g* of O_2 at 47°C ?

(*a*) $1\cdot24 \times 10^2$ J (*b*) $2\cdot24 \times 10^2$ J

(*c*) $1\cdot24 \times 10^3$ J (*d*) $3\cdot24 \times 10^2$ J

(*Orissa J.E.E. 2004*)

69. Molar volume of CO_2 is maximum at

(*a*) N.T.P. (*b*) 0°C and 2·0 atm

(*c*) 127°C and 1 atm (*d*) 273°C and 2 atm

(*J & K C.E.T. 2004*)

70. Slope of the plot between PV and P at constant temperature is

(*a*) zero (*b*) 1

(*c*) 1/2 (*d*) $1/\sqrt{2}$

(*Bihar C.E.C.E. 2004*)

71. The numerical value of N/*n* (where N is the number of molecules in a given sample of the gas and *n* is the number of moles of the gas) is

(*a*) 8·314 (*b*) $6\cdot02 \times 10^{23}$

(*c*) 0·0821 (*d*) $1\cdot66 \times 10^{-19}$

(*e*) $1\cdot62 \times 10^{-24}$ (*Kerala C.E.E. 2004*)

ANSWERS

57. *a,b,c*	**58.** *b,d*	**59.** *a,d*	**60.** *c*	**61.** *c*	**62.** *c*	**63.** *b*	**64.** *c*	**65.** *a*	**66.** *b*
67. *c*	**68.** *a*	**69.** *c*	**70.** *a*	**71.** *b*					

72. N_2 is found in a litre flask under 100 *k* Pa pressure and O_2 is found in another 3 litre flask under 320 *k* Pa pressure. If the two flasks are connected, the resultant pressure is

(*a*) 310 *k* Pa (*b*) 210 *k* Pa
(*c*) 420 *k* Pa (*d*) 365 *k* Pa
[✓ (*e*) 265 *k* Pa] *(Kerala M.E.E. 2004)*

73. Triple point of water is

(*a*) 273 K (*b*) 373 K
(*c*) 203 K (*d*) 193 K *(A.F.M.C. 2004)*

74. Which of the following statement about amorphous solids is incorrect ?

(*a*) They melt over a range of temperature
[✓ (*b*) They are anisotropic]
(*c*) There is no orderly arrangement of particles
(*d*) They are rigid and incompressible *(Karnataka C.E.T. 2004)*

75. At a certain pressure, volume of the gas at 27°C is 20 litre. If the pressure and temperature are doubled, the volume will be

(*a*) 40 litre [✓ (*b*) 20 litre]
(*c*) 10·9 litre (*d*) 8·2 litre *(U.P. C.P.M.T. 2004)*

HINTS/EXPLANATIONS to Multiple Choice Questions

3. $r_{H_2}/r_{D_2} = \sqrt{4/2} = \sqrt{2} = 1{\cdot}414$. This is the maximum difference in the rate of diffusion out of the given pairs.

5. $r \propto 1/\sqrt{M}$. Molecular mass of HCl (36·5) is greater than that of NH_3 (17), hence HCl will diffuse slowly *i.e.* the ring will be formed near the HCl bottle.

6. $$\frac{r_{CH_4}}{r_X} = \sqrt{\frac{M_X}{M_{CH_4}}} \quad \textit{i.e.} \quad 2 = \sqrt{\frac{M_X}{16}}$$

or $M_X = 64{\cdot}0$

7. Higher the pressure and lower the temperature, greater is the density.

9. Kinetic energy of any gas per mole $= \frac{3}{2}$ RT.

11. $w_{H_2} = w_{C_2H_6} = w$ g

$\therefore \; n_{H_2} = w/2, n_{C_2H_6} = w/30$

$$x_{H_2} = \frac{w/2}{w/2 + w/30} = \frac{1/2}{1/2 + 1/30}$$

$$= \frac{1}{2} \times \frac{30}{16} = \frac{30}{32} = \frac{15}{16}$$

$$p_{H_2} = x_{H_2} \times P_{total} = (15/16) \times P_{total}$$

12. $D_A/D_B = \sqrt{\rho_B/\rho_A}$ *i.e.* $D_A = D_B(\rho_B/\rho_A)^{1/2}$

15. Under similar conditions of temperature and pressure, equal volumes of different gases contain equal number of moles.

$\therefore$ Masses of O_2, Ne and CH_4 will be in the ratio 32 : 20 : 16.

17. Pressure of dry gas, P = *n*RT/V

$= 0{\cdot}0168 \times (0{\cdot}0821 \times 1000 \times 760 \text{ ml } mm) \times 298/428 = 730 \, mm$

Pressure of moist gas = 754 *mm*. Hence pressure of water vapour = (754—730) *mm* = 24 *mm*.

Alternatively, volume of 0·0168 mol of O_2 at STP $= 0{\cdot}0168 \times 22400 = 376{\cdot}3$ ml

Thus $V_1 = 376{\cdot}3$ ml, $P_1 = 760$ mm, $T_1 = 273$ K

$V_2 = 428$ ml, $P_2 = ?$, $T_2 = 298$ K.

Calculate P_2.

18. Vapour pressure of a liquid depends only on temperature and not on the volume of the container or the liquid.

19. $$u = \sqrt{\frac{3RT}{M}}$$

$$\therefore \; \frac{u_{H_2}}{u_{O_2}} = \sqrt{\frac{T_{H_2}}{M_{H_2}} \times \frac{M_{O_2}}{T_{O_2}}} = \sqrt{\frac{50}{2} \times \frac{32}{800}} = 1$$

20. $$\frac{r_{H_2}}{r_X} = \sqrt{\frac{M_X}{M_{H_2}}}$$

or $$\frac{X/5}{X/t} = \sqrt{\frac{M_X}{2}}$$

or $$\frac{t}{5} = \sqrt{\frac{M_X}{2}}$$

The equality holds good only for (*b*).

22. Polar molecules (like H_2O) have dipole moment. As a result intermolecular forces of attraction are greater and so is the critical temperature.

ANSWERS

72. *e* **73.** *a* **74.** *b* **75.** *b*

23. $r \propto P$ and $\propto 1/\sqrt{d}$ or $\propto 1/\sqrt{M}$.

Hence $\dfrac{r_A}{r_B} = \dfrac{P_A}{P_B}\left(\dfrac{M_B}{M_A}\right)^{1/2}$

24. Mass of the gas is determined by weighing the container containing the gas and then the empty container.

25. K.E. of a gas depends only on temperature.

26. $\dfrac{r_{O_2}}{r_{H_2}} = \dfrac{u_{O_2}}{u_{H_2}} = \sqrt{\dfrac{d_{H_2}}{d_{O_2}}} = \sqrt{\dfrac{1}{16}} = 1:4$

27. $n_{O_2} = 4/32 = 1/8$ mol, $n_{H_2} = 2/2$ mol $= 1$ mol,

Total $n = 9/8$ mol

$PV = nRT$ or $P = nRT/V$

$= (9/8) \times (0{\cdot}0821)(273)/1 = 25{\cdot}215$ atm.

29. $V_1/T_1 = V_2/T_2$ *i.e.* $300/300 = V_2/280$

or $V_2 = 280$ ml

30. $P_1V_1/T_1 = P_2V_2/T_2$

i.e. $(1 \times 100)/273 = (1{\cdot}5 \times V_2)/(273 + 91)$

or $V_2 = 88{\cdot}9$ c.c.

31. Mol. mass of air = Mass of 22400 cc at STP

$= 0{\cdot}00130 \times 22400 = 29{\cdot}12$.

V.D. = Mol. mass/2.

32. Clausius-Clapeyron equation is

$$\log\frac{P_2}{P_1} = \frac{\Delta H_v}{2{\cdot}303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

33. $PV = nRT = \dfrac{w}{M}RT$

or $P = \dfrac{w}{V}\dfrac{RT}{M} = \dfrac{dRT}{M}$

Thus $P \propto d$, $P \propto T$. Hence

$$\frac{P_1}{P_2} = \frac{d_1}{d_2} \times \frac{T_1}{T_2} = \frac{1}{2} \times \frac{2}{1} = 1:1.$$

34. $PV = nRT$ is obeyed by an *ideal gas*, the process may be isothermal or adiabatic.

35. $r_X/r_{N_2} = \sqrt{M_{N_2}/M_X} = \sqrt{28/56}$

$= \sqrt{1/2} = 1/\sqrt{2}$.

or $r_{N_2} = r_X \times \sqrt{2} = 56 \times \sqrt{2} = 79{\cdot}19\ \text{ml}\,s^{-1}$

36. The variation of volume with temperature (at constant pressure) is governed by Charles law.

37. Mass of 22·4 L of the gas at STP = Gram Molecular mass.

38. $u = \sqrt{\dfrac{3RT}{M}}$,

$\dfrac{u(H_2)}{u(N_2)} = \sqrt{\dfrac{T(H_2)}{M(H_2)} \times \dfrac{M(N_2)}{T(N_2)}}$,

$\sqrt{7} = \sqrt{\dfrac{T(H_2)}{T(N_2)} \times \dfrac{28}{2}}$,

$7 = \dfrac{T(H_2)}{T(N_2)} \times 14$

or $T(N_2) = 2\,T(H_2)$

i.e. $T(N_2) > T(H_2)$

or $T(H_2) < T(N_2)$.

39. $Z = \dfrac{PV}{nRT}$ *i.e.* $\dfrac{PV}{nRT} < 1$

or $PV < nRT$

or $1\ \text{atm} \times V < 1 \times 0{\cdot}0821 \times 273$

or $V < 22{\cdot}4$ litres.

40. Mass of 1 L steam $= 1000 \times 0{\cdot}0006 = 0{\cdot}6\,g$ = Mass of liquid water. Vol. of water = 0·6 cc. Same volume will be occupied by water molecules in steam.

42. $u = \sqrt{\dfrac{3RT}{M}}$

When $u_{SO_2} = u_{O_2}$,

then $\dfrac{T_{SO_2}}{M_{SO_2}} = \dfrac{T_{O_2}}{M_{O_2}}$

or $\dfrac{T_{SO_2}}{64} = \dfrac{303}{32}$

or $T_{SO_2} = 606$ K

43. $u = \sqrt{\dfrac{3RT}{M}}$ $\therefore$ $\dfrac{u_{CO_2}}{u_{N_2O}} = \sqrt{\dfrac{T_{CO_2}}{M_{CO_2}} \times \dfrac{M_{N_2O}}{T_{N_2O}}}$

i.e. $\dfrac{x}{4x} = \sqrt{\dfrac{T}{44} \times \dfrac{44}{T_{N_2O}}}$

or $T_{N_2O} = 16\,T$

44. Lower the density of the gas, faster it will be filled. As H_2 has lowest density, it will be filled first.

45. At sea level, atmospheric pressure is high. Hence air has high density. This is an application of Boyle's law.

46. $u = \sqrt{\frac{3\,RT}{M}}$. At constant T, $u \propto \sqrt{1/M}$. As H_2 has least molecular mass, u will be maximum for H_2.

49. $PV = nRT$ or $\frac{n}{V} = \frac{P}{RT}$

i.e. no. of moles per litre = P/RT.

50. Some covalent solids like SiO_2 (quartz), SiC, diamond and graphite have very high melting points (~ 4000 K).

52. Volume of 1 mole of an ideal gas at 273 K and 1 atm is 22·4 L. Volume at 373 K and 1 atm pressure will be

$$V = \frac{RT}{P} = \frac{0 \cdot 082 \times 373}{1} = 30 \cdot 58\ L \approx 30 \cdot 6\ L.$$

54. Deviations from ideal behaviour are expressed in terms of compressibility factor, $Z = \frac{PV}{nRT}$.

From positive deviations, Z > 1.

55. Initially, partial pressures were equal. As $r \propto \sqrt{1/d}$ or $\sqrt{1/M}$, therefore amounts diffused out in the same time will be $H_2 > CH_4 > SO_2$. Amounts left will be $H_2 < CH_4 < SO_2$ or $SO_2 > CH_4 > H_2$. Hence $p_{SO_2} > p_{CH_4} > p_{H_2}$.

56. $u = \sqrt{\frac{3\,RT}{M}} = \sqrt{\frac{3\,PV}{M}}$.

As temperature is constant, PV is constant. Hence *r.m.s.* is constant even if pressure is doubled.

58. According to Boyle's law, PV = K at constant T.

$\therefore\ P = K/V$ or $(dP/dV)_T = -K/V^2$.

Also $V \propto 1/P$.

59. According to Charle's law, $\frac{V}{T} = K$ at constant P.

or $V = KT$ or $(dV/dT)_P = K$. Also $V \propto T$.

60. R.M.S. of one mole of a monoatomic gas is

$$U_{r.m.s.} = \sqrt{\frac{3\,RT}{M}}$$

Average K.E. is $E = \frac{3}{2}RT$ or $2\,E = 3\,RT$ $\therefore$

$$U_{r.m.s.} = \sqrt{\frac{2\,E}{M}}.$$

61. For monoatomic neon atoms, $E = \frac{3}{2}RT$

$$\therefore \frac{E_{40^\circ}}{E_{20^\circ}} = \frac{T_{40^\circ}}{T_{20^\circ}} = \frac{40 + 273}{20 + 273} = \frac{313}{293}.$$

62. '*b*' is volume correction factor. It is a measure of the effective volume occupied by the gas molecules.

63. For B, $P_1 = P$, $V_1 = V$, $T_1 = T$. For A, $P_1 = 2\,P$, $V_2 = 2\,P$, $T_2 = 2\,T$

Applying ideal gas equation, $PV = n\,RT$.

$$\frac{P_1\,V_1}{n_1\,RT_1} = \frac{P_2\,V_2}{n_2\,RT_2} \text{ or } \frac{PV}{n_1\,RT} = \frac{2\,P \times 2\,V}{n_2\,R\,(2\,T)}$$

$$\text{or } \frac{n_2}{n_1} = \frac{2}{1}$$

64. $\frac{P_1\,V_1}{T_1} = \frac{P_2\,V_2}{T_2}$ *i.e.* $\frac{P \times 4}{T} = \frac{2\,P \times V_2}{2\,T}$

or $V_2 = 4\ dm^3$.

65. $\frac{r_{H_2}}{r_A} = \sqrt{\frac{M_A}{M_{H_2}}}$ $\therefore 6 = \sqrt{\frac{M_A}{2}}$ or $M_A = 72$.

66. $\left(P + \frac{an^2}{V}\right)(V - nb) = n\,RT$

$$\text{or } P = \frac{n\,RT}{V - nb} - \frac{an^2}{V^2}$$

$$= \frac{2 \times 0 \cdot 0821 \times 300}{5 - 2 \times 0 \cdot 03711} - \frac{4 \cdot 17 \times 2^2}{5^2}$$

$$= 10 - 0 \cdot 66 = 9 \cdot 33\ atm.$$

67. $\frac{\alpha}{v} = \frac{\sqrt{2\,RT/M}}{\sqrt{8\,RT/\pi\,M}} = \frac{\sqrt{2\,\pi}}{\sqrt{8}} = \frac{\sqrt{2\,\pi}}{2\,\sqrt{2}} = \frac{\sqrt{\pi}}{2}$.

68. $K.E. = \frac{3}{2}n\,RT = \frac{3}{2}\frac{w}{M}RT$

$$= \frac{3}{2} \times \frac{1}{32} \times 8 \cdot 314 \times 320\ J = 1 \cdot 24 \times 10^2\ J.$$

69. $PV = RT$ or $V = \frac{RT}{P}$. Greater the value of T/P, greater is the volume.

70. Plot is a horizontal line. Hence slope = 0.

71. N/*n* represents the no. of molecules per mole of the gas *i.e.* Avogadro's no.

72. $P_1\,V_1 + P_2\,V_2 = P_3\,(V_1 + V_2)$,

$100 \times 1 + 320 \times 3 = P_3\,(1 + 3)$

or $P_3 = 265\ k\,Pa$

73. Triple point of water is the temperature at which all the three phases ice-water-vapour coexist. It is 0·01°C = 273·16 K at 4·58 mm pressure.

75. $P_1 = P$, $V_1 = 20\ L$, $T_1 = T$

$P_2 = 2\,P$, $V_2 = ?$, $T_2 = 2\,T$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2},\ \frac{P \times 20}{T} = \frac{2\,P \times V_2}{2\,T},\ V_2 = 20\ L.$$

ADDITIONAL QUESTIONS

For All Competitive Examinations

Assertion-Reason Type Questions

The following questions consist of two statements each, printed as Assertion and Reason. While answering these questions you are required to choose any one of the following five responses.

(*a*) If both Assertion and Reason are true and the Reason is correct explanation of the Assertion.

(*b*) If both Assertion and Reason are true and the Reason is not the correct explanation of the Assertion.

(*c*) If Assertion is true but the Reason is false.

(*d*) If Assertion is false but the Reason is true.

(*e*) If both Assertion and Reason are false.

	Assertion	Reason
1.	For a certain fixed amount of gas, the product PV is always constant.	Real gases deviate from ideal behaviour at low pressure and high temperatures.
2.	Different gases at the same conditions of temperature and pressure have same root mean square velocity.	Average kinetic energy of a gas is directly proportional to temperature in Kelvin scale.
3.	At zero degree Kelvin the volume occupied by a gas is negligible.	All molecular motion ceases at 0 K.
4.	The pressure of real gases is less than the pressure of the ideal gas.	The intermolecular forces of attraction in real gases are greater than those of ideal gas.
5.	The pressure of a fixed amount of an ideal gas is proportional to its temperature.	Frequency of colloisions and their impact both increase in proportion to the square root of the temperature.
6.	Latent heat of fusion of solid carbon dioxide is much less than that of SiO_2.	SiO_2 exists as a discrete molecule.
7.	Liquefaction of H_2 and He is difficult.	Critical temperatures of H_2 and He gases are high.
8.	The value of van der Waals constant '*a*' is higher for ammonia than for nitrogen.	Intermolecular hydrogen bonding is present in ammonia. ***(I.I.T. 1998)***
9.	Effusion rate of oxygen is smaller than nitrogen.	Molecular size of nitrogen is smaller than oxygen. ***(A.I.I.M.S. 2004)***

True/False Statements

Which of the following statements are false ? Rewrite them correctly.

1. The graph between PV vs. P at constant temperature is linear parallel to the pressure axis.
2. Volume remaining constant, pressure is inversely proportional to temperature in degrees kelvin.
3. Real gases show deviation from ideal behaviour at low temperature and high pressures.
4. In the microscopic model of the gas, all the molecules are supposed to move with the same velocities.
5. A liquid gets heated up when it evaporates.
6. Mercury rises in a capillary tube.
7. A liquid which has high coefficient of viscosity has low fluidity.
8. Glass possesses fluidity.
9. Crystalline solids are isotropic.
10. In a gas, intermolecular forces of attraction are weakest while thermal energy is highest.
11. In the van der Waal's equation

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

the constant '*a*' represents the actual volume of the gas molecules. ***(I.I.T. 1993)***

12. A mixture of ideal gases is cooled upto liquid helium temperature (4·22 K) to form an ideal solution. ***(I.I.T. 1996)***

Fill In The Blanks

1. 1 L = ... dm^3.
2. 1 bar = ... N m^{-2}.
3. The instrument used for the measurement of pressure of a gas is called .....
4. The absolute scale of temperature was given by ....
5. A graph between volume (in L) vs. temperature (in °C) at constant pressure on extrapolation cuts the temperature axis at .....
6. Aqueous tension is the vapour pressure of ..... and depends only upon ..... .
7. The model used to explain the properties of gases is called .....
8. Boiling point is the temperature at which the vapour pressure becomes equal to .....
9. Fluidity is ..... of viscosity.
10. The crystalline parts of the amorphous solids are called .....
11. The SI unit of viscosity is........
12. 1 poise = ...th of SI unit.
13. Solid NaCl is a ..... conductor of electricity. *(Roorkee 1990)*
14. The absolute temperature of an ideal gas is.......... to/than the average kinetic energy of the gas molecules. *(I.I.T. 1997)*
15. A liquid which is permanently supercooled is frequently called a.......... *(I.I.T. 1997)*

Matching Type Questions

Match the entries of column A with appropriate entries of column B

Column A	**Column B**
1. Root mean square speed ($u_{r.m.s.}$)	1. $\sqrt{\frac{RT}{M}}$
2. Average speed (u_{av})	2. $\sqrt{\frac{3\,RT}{M}}$
3. Most probable speed (u_{mp})	3. $\sqrt{\frac{8\,RT}{\pi\,M}}$
4. Kinetic energy per mole	4. $\frac{3}{2}RT$

ANSWERS

ASSERTION-REASON TYPE QUESTIONS

1. *d* **2.** *d* **3.** *c* **4.** *a* **5.** *a* **6.** *c* **7.** *c* **8.** *a* **9.** *c*

TRUE/FALSE STATEMENTS

2, 4, 5, 6, 9, 11, 12. (ideal gases cannot be liquefied above 0K)

FILL IN THE BLANKS

1. one **2.** 10^5 **3.** manometer **4.** Lord Kelvin **5.** —273°C **6.** water vapours, temperature **7.** Microscopic model **8.** external pressure (atmospheric pressure) **9.** reciprocal **10.** crystallites **11.** $Nm^{-2}s$ or Pa s or kg $m^{-1}s^{-1}$ **12.** $\frac{1}{10}$ **13.** Poor **14.** directly proportional to **15.** glass.

MATCHING TYPE QUESTIONS

1—2, 2—3, 3—1, 4—4.

HINTS/EXPLANATIONS to Assertion-Reason Type Questions

2. $u = \sqrt{3\,RT / M}$. So u depends not only on T but also on M.
3. Vibratory motion exists even at 0 K.
7. Critical temperatures of H_2 and He gases are low.
9. Molecular size decreases from left to right along a period. Thus, molecular size of nitrogen is greater than oxygen.