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10

Gaseous State

CHAPTER

CONTENTS

All matter exists in three states: *gas*, *liquid* and *solid*. A molecular level representation of gaseous, liquid and solid states is shown in Fig. 10.1

A **gas** consists of molecules separated wide apart in empty space. The molecules are free to move about throughout the container.

A **liquid** has molecules touching each other. However, the intermolecular space, permit the movement of molecules throughout the liquid.

A **solid** has molecules, atoms or ions arranged in a certain order in fixed positions in the crystal lattice. The particles in a solid are not free to move about but vibrate in their fixed positions.

Of the three states of matter, the gaseous state is the one most studied and best understood. We shall consider it first.

GENERAL CHARACTERISTICS OF GASES

1. Expansibility

Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.

2. Compressibility

Gases are easily compressed by application of pressure to a movable piston fitted in the container.

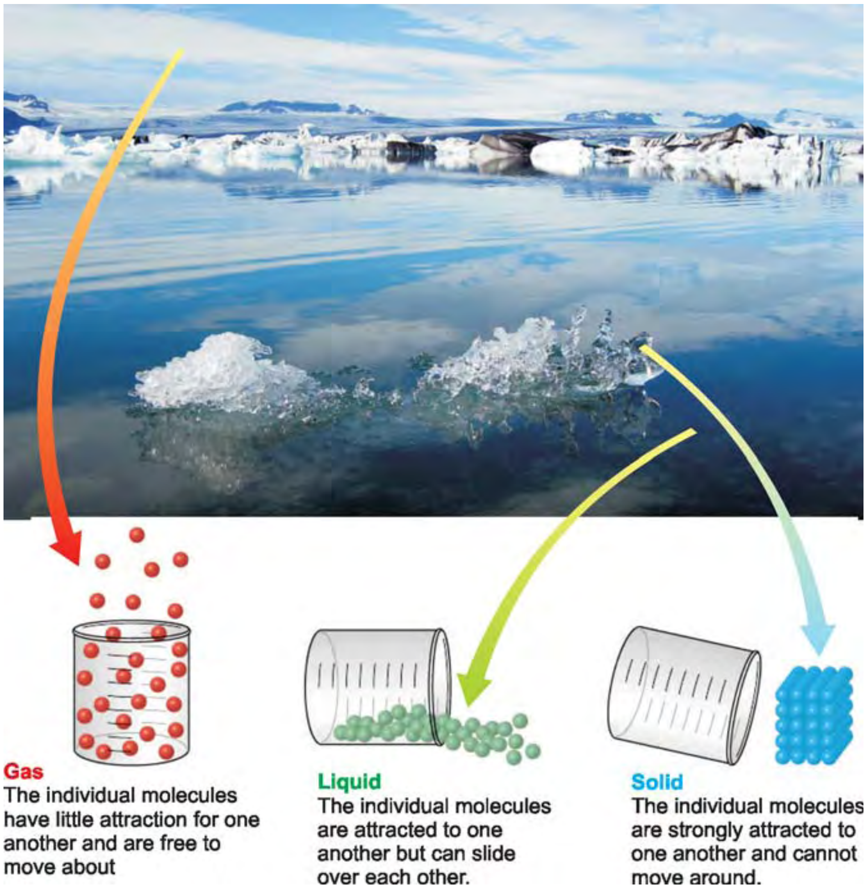

Figure 10.1
Molecular representation of the gaseous, liquid and solid states.

3. Diffusibility

Gases can diffuse rapidly through each other to form a homogeneous mixture.

4. Pressure

Gases exert pressure on the walls of the container in all directions.

5. Effect of Heat

When a gas, confined in a vessel is heated, its pressure increases. Upon heating in a vessel fitted with a piston, volume of the gas increases.

The above properties of gases can be easily explained by the Kinetic Molecular Theory which will be considered later in the chapter.

PARAMETERS OF A GAS

A gas sample can be described in terms of four parameters (measurable properties):

(1) the volume, V of the gas
(2) its pressure, P
(3) its temperature, T
(4) the number of moles, n, of gas in the container

The Volume, *V*

The volume of the container is the volume of the gas sample. It is usually given in litre (l or L) or millilitres (ml or mL).

$$1 \text{ litre(l)} = 1000 \text{ ml and } 1 \text{ ml} = 10^{-3} \text{ l}$$

One millilitre is practically equal to one cubic centimetre (cc). Actually

$$1 \text{ litre(l)} = 1000.028 \text{ cc}$$

The SI unit for volume is cubic metre (m^3) and the smaller unit is decimeter^3 (dm^3).

The pressure of a gas is defined as the force exerted by the impacts of its molecules per unit surface area in contact. The pressure of a gas sample can be measured with the help of a mercury manometer (Fig. 10.2) Similarly, the atmospheric pressure can be determined with a mercury barometer (Fig. 10.3).

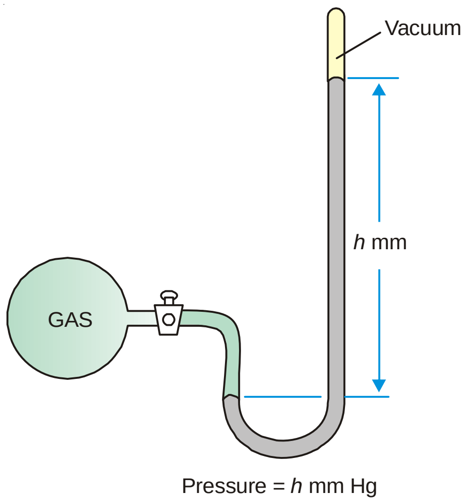

Figure 10.2
A mercury manometer.

The gas container is connected with a U-tube containing Hg having vacuum in the closed end. The difference in Hg height in two limbs gives the gas pressure in mm Hg.

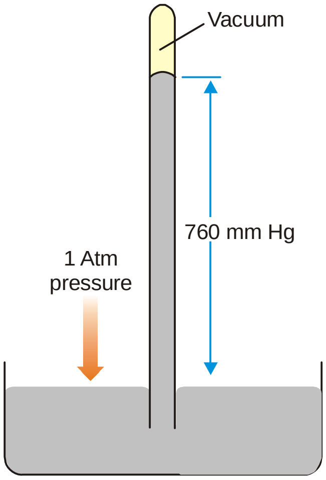

Figure 10.3
A mercury barometer.

A long tube (80 × 1 cm) filled with Hg inverted into dish containing Hg. The atmospheric pressure is equal to 760 mm Hg column supported by it at sea level.

The pressure of air that can support 760 mm Hg column at sea level, is called one atmosphere (1 atm). The unit of pressure, millimetre of mercury, is also called **torr.**

Thus,

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

The SI unit of pressure is the **Pascal** (Pa). The relation between atmosphere, torr and pascal is :

$$1 \text{ atm} = 760 \text{ torr} = 1.013 \times 10^5 \text{ Pa}$$

The unit of pressure 'Pascal" is not in common use.

Temperature, *T*

The temperature of a gas may be measured in **Centigrade degrees** (°C) or **Celsius degrees.** The SI unit of temperature is **Kelvin (K)** or **Absolute degree.** The centigrade degrees can be converted to **kelvins** by using the equation.

$$K = °C + 273$$

The Kelvin temperature (or absolute temperature) is always used in calculations of other parameters of gases. **Remember that the degree sign (°) is not used with K**.

The Moles of a Gas Sample, *n*

The number of moles, *n*, of a sample of a gas in a container can be found by dividing the mass, *m*, of the sample by the molar mass, *M* (molecular mass).

$$\text{moles of gas } (n) = \frac{\text{mass of gas sample } (m)}{\text{molecular mass of gas } (M)}$$

THE GAS LAWS

The volume of a given sample of gas depends on the temperature and pressure applied to it. Any change in temperature or pressure will affect the volume of the gas. As results of experimental studies from 17th to 19th century, scientists derived the relationships among the pressure, temperature and volume of a given mass of gas. These relationships, which describe the general behaviour of gases, are called the **gas laws.**

BOYLE'S LAW

In 1660 Robert Boyle found out experimentally the change in volume of a given sample of gas with pressure at room temperature. From his observations he formulated a generalisation known as **Boyle's Law.** It states that : **at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure. If the pressure is doubled, the volume is halved.**

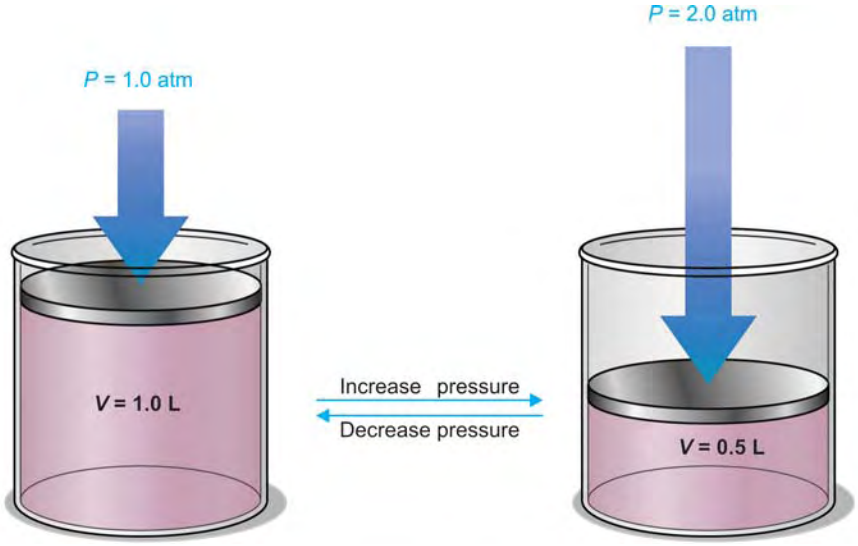

Figure 10.4
Boyle's law states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure. If the pressure is doubled, the volume is halved.

The Boyle's Law may be expressed mathematically as

$$V \propto 1/P \qquad (T, n \text{ are constant})$$

or

$$V = k \times 1/P$$

where *k* is a proportionality constant.

$$PV = k$$

If P_1, V_1 are the initial pressure and volume of a given sample of gas and P_2, V_2 the changed pressure and volume, we can write

$$P_1 V_1 = k = P_2 V_2$$

or $$P_1 V_1 = P_2 V_2$$

This relationship is useful for the determination of the volume of a gas at any pressure, if its volume at any other pressure is known.

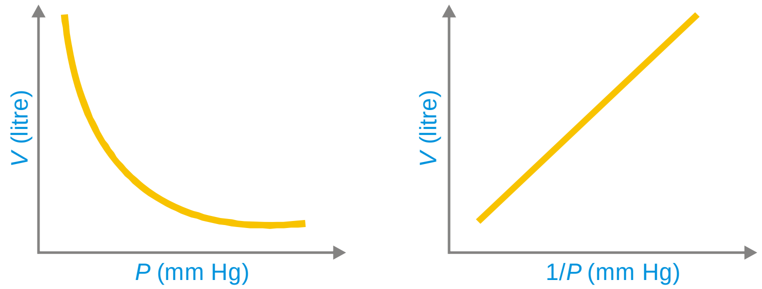

Figure 10.5

Graphical representation of Boyle's law. (*a*) a plot of *V* versus *P* for a gas sample is hyperbola; (*b*) a plot of *V* versus 1/*P* is a straight line.

The Boyle's law can be demonstrated by adding liquid mercury to the open end of a J-tube. As the pressure is increased by addition of mercury, the volume of the sample of trapped gas decreases. Gas pressure and volume are inversely related; one increases when the other decreases.

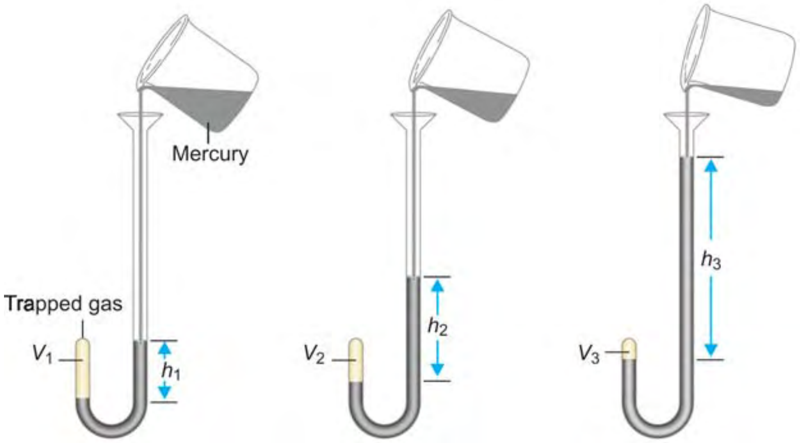

Figure 10.6

Demonstration of Boyle's law.

CHARLES'S LAW

In 1787 Jacques Charles investigated the effect of change of temperature on the volume of a fixed amount of gas at constant pressure. He established a generalisation which is called the **Charles' Law.** It states that : **at constant pressure, the volume of a fixed mass of gas is directly proportional to the Kelvin temperature of absolute temperature. If the absolute temperature is doubled, the volume is doubled.**

Charles' Law may be expressed mathematically as

$$V \propto T \qquad (P, n \text{ are constant})$$

or $$V = k\,T$$

where k is a constant.

or

$$\frac{V}{T} = k$$

If V_1, T_1 are the initial volume and temperature of a given mass of gas at constant pressure and V_2, T_2 be the new values, we can write

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

or

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

Using this expression, the new volume V_2, can be found from the experimental values of V_1, T_1 and T_2.

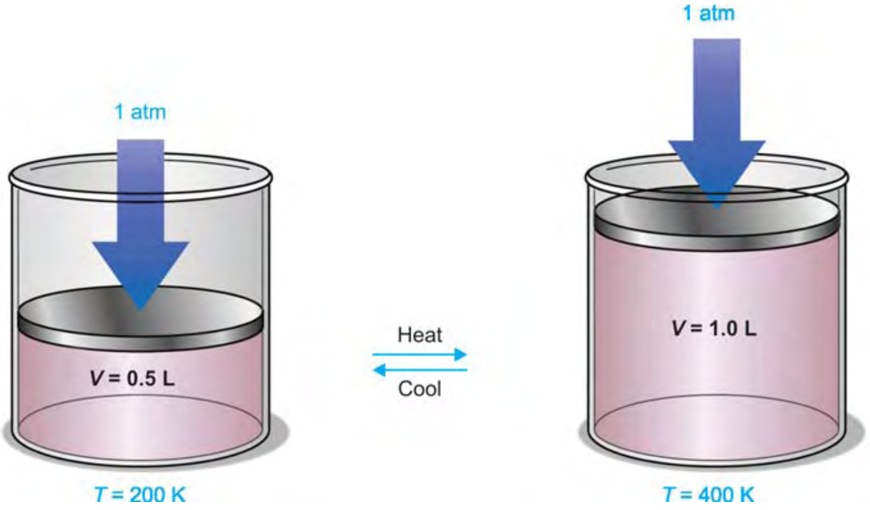

Figure 10.7
Charles law state that at constant pressure, the volume of a fixed mass of gas is directly proportional to the absolute temperature.

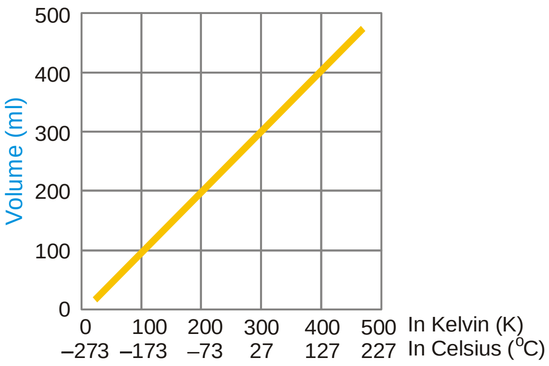

Figure 10.8
Graph showing that at constant pressure, volume of a given mass of gas is directly proportional to the Kelvin temperature.

THE COMBINED GAS LAW

Boyle's Law and Charles' Law can be combined into a single relationship called the **Combined Gas Law.**

Boyle's Law $V \propto \frac{1}{P}$ (T, n constant)

Charles' Law $V \propto T$ (P, n constant)

Therefore, $V \propto \frac{T}{P}$ (n constant)

The combined law can be stated as : **for a fixed mass of gas, the volume is directly proportional to kelvin temperature and inversely proportional to the pressure.**

If k be the proportionality constant,

$$V = \frac{kT}{P} \quad (n \text{ constant})$$

or

$$\frac{PV}{T} = k \quad (n \text{ constant})$$

If the pressure, volume and temperature of a gas be changed from P_1, V_1 and T_1 to P_2, T_2 and V_2, then

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

or

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

This is the form of combined law for two sets of conditions. It can be used to solve problems involving a change in the three variables P, V and T for a fixed mass of gas.

SOLVED PROBLEM. 25.8 litre of a gas has a pressure of 690 torr and a temperature of 17°C. What will be the volume if the pressure is changed to 1.85 atm and the temperature to 345 K.

SOLUTION

Initial conditions :	*Final Conditions :*
$V_1 = 25.8$ litres	$V_2 = ?$
$P_1 = \frac{690}{760} = 0.908$ atm	$P_2 = 1.85$ atm
$T_1 = 17 + 273 = 290$ K	$T_2 = 345$ K

Substituting values in the equation

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

$$\frac{0.908 \text{ atm} \times 25.8 \text{ litre}}{290 \text{ K}} = \frac{1.85 \text{ atm} \times V_2}{345 \text{ K}}$$

Hence,

$$V_2 = \frac{0.908 \times 25.8 \times 345}{290 \times 1.85} = \mathbf{15.1 \text{ litres}}$$

GAY LUSSAC'S LAW

In 1802 Joseph Gay Lussac as a result of his experiments established a general relation between the pressure and temperature of a gas. This is known as **Gay Lussac's Law or Pressure-Temperature Law.** It states that : **at constant volume, the pressure of a fixed mass of gas is directly proportional to the Kelvin temperature or absolute temperature.**

The law may be expressed mathematically as

$$P \propto T \qquad \text{(Volume, } n \text{ are constant)}$$

or $$P = kT$$

or $$\frac{P}{T} = k$$

For different conditions of pressure and temperature

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

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

Knowing P_1, T_1, and T_2, P_2 can be calculated.

AVOGADRO'S LAW

Let us take a balloon containing a certain mass of gas. If we add to it more mass of gas, holding the temperature (T) and pressure (P) constant, the volume of gas (V) will increase. It was found experimentally that the amount of gas in moles is proportional to the volume. That is,

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

or $$V = An$$

where A is constant of proportionality.

or $$\frac{V}{n} = A$$

For any two gases with volumes V_1, V_2 and moles n_1, n_2 at constant T and P,

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

If $$V_1 = V_2, \qquad n_1 = n_2$$

Thus for equal volumes of the two gases at fixed T and P, number of moles is also equal. This is the basis of **Avogadro's Law** which may be stated as : **equal volumes of gases at the same temperature and pressure contain equal number of moles or molecules. If the molar amount is doubled, the volume is doubled.**

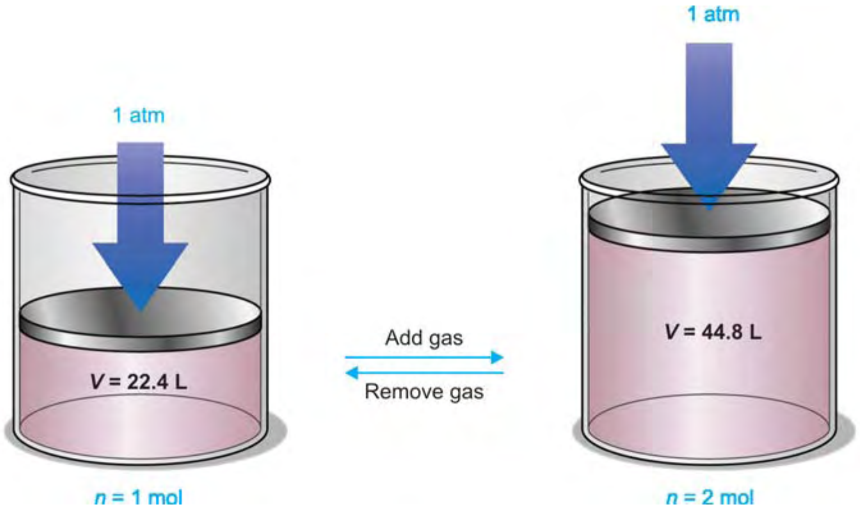

Figure 10.9
Avogadro's law states that under equal conditions of temperature and pressure, equal volumes of gases contain an equal number of molecules.

The Molar Gas Volume. It follows as a corollary of Avogadro's Law that one mole of any gas at a given temperature (T) and pressure (P) has the same fixed volume. It is called the molar gas volume or **molar volume.** In order to compare the molar volumes of gases, chemists use a fixed reference temperature and pressure. This is called standard temperature and pressure (abbreviated, **STP**). The standard temperature used is 273 K (0°C) and the standard pressure is 1 atm (760 mm Hg). At STP we find experimentally that one mole of any gas occupies a volume of 22.4 litres. To put it in the form of an equation, we have

$$1 \text{ mole of a gas at STP} = 22.4 \text{ litres}$$

THE IDEAL GAS EQUATION

We have studied three simple gas laws :

Boyle's Law	$V \propto \dfrac{1}{P}$	(T, n constant)
Charles' Law	$V \propto T$	(n, P constant)
Avogadro's Law	$V \propto n$	(P, T constant)

These three laws can be combined into a single more general gas law :

$$V \propto \frac{nT}{P} \qquad \text{...(1)}$$

This is called the **Universal Gas Law.** It is also called **Ideal Gas Law** as it applies to all gases which exhibit ideal behaviour *i.e.*, obey the gas laws perfectly. The ideal gas law may be stated as : **the volume of a given amount of gas is directly proportional to the number of moles of gas, directly proportional to the temperature, and inversely proportional to the pressure.**

Introducing the proportionality constant R in the expression (1) we can write

$$V = R\frac{nT}{P}$$

or $$PV = nRT \qquad \text{...(2)}$$

The equation (2) is called the **Ideal-gas Equation** or simply the general **Gas Equation.** The constant R is called the **Gas constant.** The ideal gas equation holds fairly accurately for all gases at low pressures. For one mole ($n = 1$) of a gas, the ideal-gas equation is reduced to

$$PV = RT \qquad \text{...(3)}$$

The ideal-gas equation is called an **Equation of State** for a gas because it contains all the variables (T, P, V and n) which describe completely the condition or state of any gas sample. If we know the three of these variables, it is enough to specify the system completely because the fourth variable can be calculated from the ideal-gas equation.

The Numerical Value of *R*. From the ideal-gas equation, we can write

$$R = \frac{PV}{nT} \qquad \text{...(1)}$$

We know that one mole of any gas at STP occupies a volume of 22.4 litres. Substituting the values in the expression (1), we have

$$R = \frac{1 \text{ atm} \times 22.4 \text{ litres}}{1 \text{ mole} \times 273 \text{ K}}$$

$$= 0.0821 \text{ atm. litre mol}^{-1} \text{ K}^{-1}$$

It may be noted that the unit for R is complex; it is a composite of all the units used in calculating the constant.

If the pressure is written as force per unit area and volume as area times length, from (1)

$$R = \frac{(\text{force/area}) \times \text{area} \times \text{length}}{n \times T} = \frac{\text{force} \times \text{length}}{n \times T}$$

$$= \frac{\text{work}}{n\,T}$$

Hence R can be expressed in units of work or energy per degree per mole. The actual value of R depends on the units of P and V used in calculating it. The more important values of R are listed in Table 10.1.

TABLE 10.1. VALUE OF **R** IN DIFFERENT UNITS

0.0821	litre-atm K^{-1} mol^{-1}	8.314×10^7	erg K^{-1} mol^{-1}
82.1	ml-atm K^{-1} mol^{-1}	8.314	Joule K^{-1} mol^{-1}
62.3	litre-mm Hg K^{-1} mol^{-1}	1.987	cal K^{-1} mol^{-1}

DALTON'S LAW OF PARTIAL PRESSURES

John Dalton visualised that in a mixture of gases, each component gas exerted a pressure as if it were alone in the container. The individual pressure of each gas in the mixture is defined as its **Partial Pressure.** Based on experimental evidence, in 1807, Dalton enunciated what is commonly known as the **Dalton's Law of Partial Pressures.** It states that : **the total pressure of a mixture of gases is equal to the sum of the partial pressures of all the gases present (Fig. 10.10).**

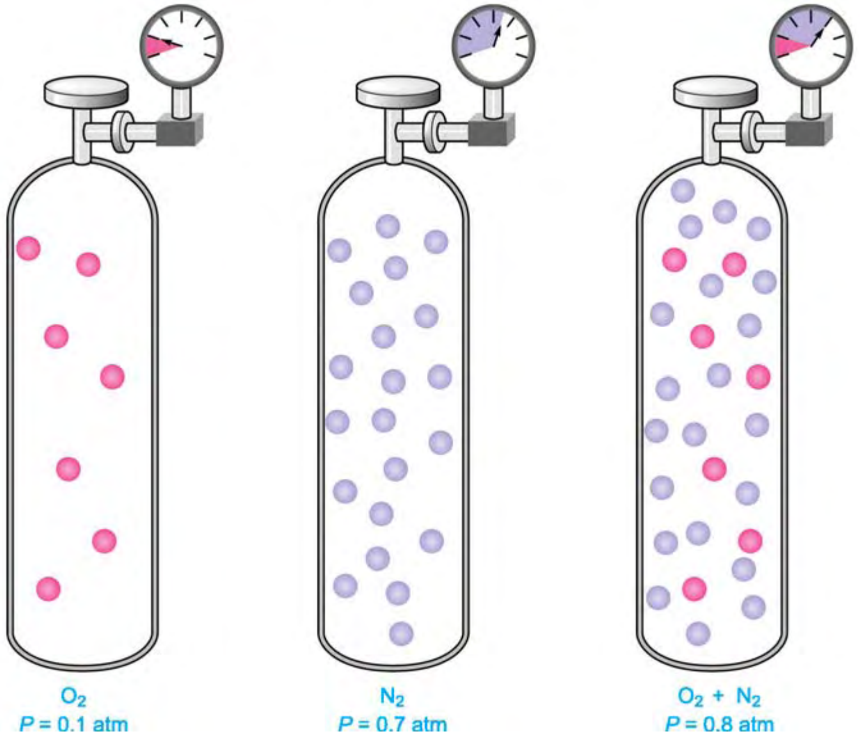

Figure 10.10
Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the partial pressures exerted by each gas. The pressure of the mixture of O_2 and N_2 (Tanks) is the sum of the pressures in O_2 and N_2 tanks.

If the pressure is written as force per unit area and volume as area times length, from (1)

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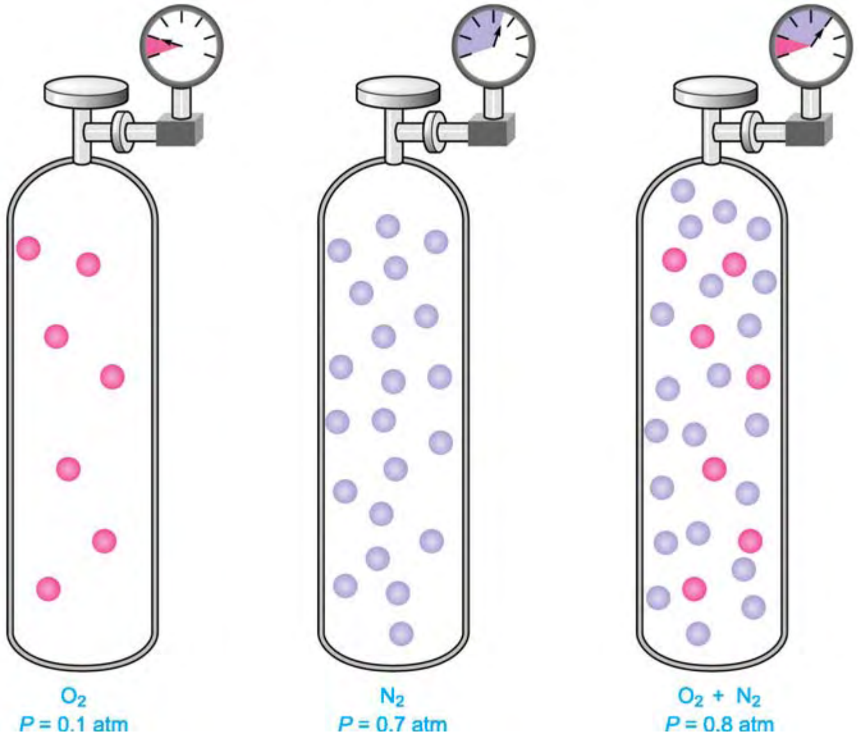


Figure 10.10
Dalton's law of partial pressures states that the total pressure of a mixture of gases is equal to the sum of the partial pressures exerted by each gas. The pressure of the mixture of O_2 and N_2 (Tanks) is the sum of the pressures in O_2 and N_2 tanks.

Mathematically the law can be expressed as $P_{total} = P_1 + P_2 + P_3$ ... (V and T are constant) where P_1, P_2 and P_3 are partial pressures of the three gases 1, 2 and 3; and so on.

Dalton's Law of Partial Pressures follows by application of the ideal-gas equation $PV = n\,RT$ separately to each gas of the mixture. Thus we can write the partial pressures P_1, P_2 and P_3 of the three gases

$$P_1 = n_1\left(\frac{RT}{V}\right) \qquad P_2 = n_2\left(\frac{RT}{V}\right) \qquad P_3 = n_3\left(\frac{RT}{V}\right)$$

where n_1, n_2 and n_3 are moles of gases 1, 2 and 3. The total pressure, P_t, of the mixture is

$$P_t = (n_1 + n_2 + n_3)\,\frac{RT}{V}$$

or

$$P_t = n_t\,\frac{RT}{V}$$

In the words, the total pressure of the mixture is determined by the total number of moles present whether of just one gas or a mixture of gases.

SOLVED PROBLEM 1. What pressure is exerted by a mixture of 2.00 g of H_2 and 8.00 g of N_2 at 273 K in a 10 litre vessel ?

SOLUTION

Applying the ideal-gas equation

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

we can find the partial pressure of H_2 and N_2

$$\text{Moles of } H_2 = \frac{2.00}{2.02} = 0.990$$

$$\text{Moles of } N_2 = \frac{8.00}{28} = 0.286$$

$$\therefore \qquad P_{H_2} = \frac{0.990 \text{ mole} \times 0.0821 \text{ atm. litre K}^{-1}\text{ mol}^{-1} \times 273 \text{ K}}{10.0 \text{ litre}}$$

$$= 2.20 \text{ atm.}$$

$$\text{and} \qquad P_{N_2} = \frac{0.286 \text{ mole} \times 0.0821 \text{ atm. litre K}^{-1}\text{ mol}^{-1} \times 273 \text{ K}}{10.0 \text{ litre}}$$

$$= 0.64 \text{ atm}$$

$$\text{Thus} \qquad P_{total} = P_{H_2} + P_{N_2}$$

$$= 2.20 \text{ atm} + 0.64 \text{ atm}$$

$$= \mathbf{2.84\ atm}$$

Thus the pressure exerted by the mixture of H_2 and N_2 is **2.84 atm.**

SOLVED PROBLEM 2. A sample of oxygen is collected by the downward displacement of water from an inverted bottle. The water level inside the bottle is equalised with that in the trough. Barometeric pressure is found to be 757 mm Hg, and the temperature of water is 23.0°C. What is the partial pressure of O_2 ? Vapour pressure of H_2O at 23°C = 19.8 mm Hg.

SOLUTION

The total pressure inside the bottle is

$$P_{\text{total}} = P_{O_2} + P_{H_2O}$$

Since the water levels inside and outside the bottle were equalised, the total gas pressure inside the bottles must be equal to P_{atm}.

$$\therefore \quad P_{\text{total}} = P_{\text{atm}} = P_{O_2} + P_{H_2O}$$

But P_{atm} is given as 757 mm Hg

$$\therefore \quad P_{O_2} = 757 \text{ mm Hg} - P_{H_2O}$$

$$= 757 \text{ mm Hg} - 19.8 \text{ mm Hg}$$

$$= \mathbf{737.2 \text{ mm Hg}}$$

Thus the partial pressure of O_2 is **737.2 mm Hg.**

GRAHAM'S LAW OF DIFFUSION

When two gases are placed in contact, they mix spontaneously. This is due to the movement of molecules of one gas into the other gas. This process of mixing of gases by random motion of the molecules is called **Diffusion.** Thomas Graham observed that molecules with smaller masses diffused faster than heavy molecules.

Figure 10.11
A light molecule diffuses quicker than a heavy molecule.

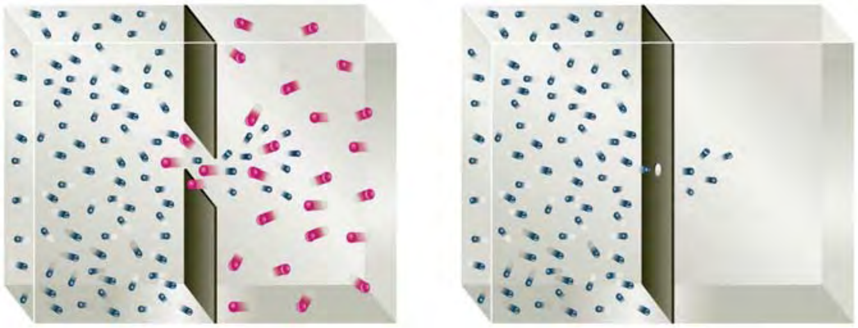
In 1829 Graham formulated what is now known as Graham's Law of Diffusion. It states that : **under the same conditions of temperature and pressure, the rates of diffusion of different gases are inversely proportional to the square roots of their molecular masses.**

Mathematically the law can be expressed as

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

where r_1 and r_2 are the rates of diffusion of gases 1 and 2, while M_1 and M_2 are their molecular masses.

When a gas escapes through a pin-hole into a region of low pressure of vacuum, the process is called **Effusion.** The rate of effusion of a gas also depends, on the molecular mass of the gas.



(a) Diffusion (b) Effusion

Figure 10.12
(*a*) Diffusion is mixing of gas molecules by random motion under conditions where molecular collisions occur. (*b*) Effusion is escape of a gas through a pinhole without molecular collisions.

Dalton's law when applied to effusion of a gas is called the Dalton's Law of Effusion. It may be expressed mathematically as

$$\frac{\text{Effusion rate of Gas 1}}{\text{Effusion rate of Gas 2}} = \sqrt{\frac{M_2}{M_1}} \qquad (P, T \text{ constant})$$

The determination of rate of effusion is much easier compared to the rate of diffusion. Therefore, Dalton's law of effusion is often used to find the molecular mass of a given gas.

SOLVED PROBLEM 1. If a gas diffuses at a rate of one-half as fast as O_2, find the molecular mass of the gas.

SOLUTION

Applying Graham's Law of Diffusion,

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

$$\frac{\frac{1}{2}}{1} = \sqrt{\frac{32}{M_1}}$$

Squaring both sides of the equation.

$$\left(\frac{1}{2}\right)^2 = \frac{32}{M_1} \text{ or } \frac{1}{4} = \frac{32}{M_1}$$

Hence, $M_1 = 128$

Thus the molecular mass of the unknown gas is **128.**

SOLVED PROBLEM 2. 50 ml of gas *A* effuse through a pin-hole in 146 seconds. The same volume of CO_2 under identical conditions effuses in 115 seconds. Calculate the molecular mass of *A*.

SOLUTION

$$\frac{\text{Effusion rate of } CO_2}{\text{Effusion rate of } A} = \sqrt{\frac{M_A}{M_{CO_2}}}$$

$$\frac{50/115}{50/146} = \sqrt{\frac{M_A}{44}}$$

or $(1.27)^2 = \frac{M_A}{44}$

Hence $M_A = 71$

∴ Molecular mass of *A* is **71.**

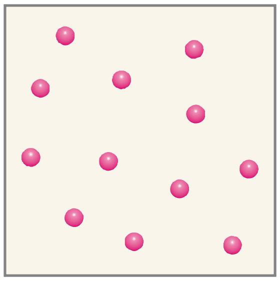
KINETIC MOLECULAR THEORY OF GASES

Maxwell and Boltzmann (1859) developed a mathematical theory to explain the behaviour of gases and the gas laws. It is based on the fundamental concept that **a gas is made of a large number of molecules in perpetual motion.** Hence the theory is called the **kinetic molecular theory** or simply the **kinetic theory of gases** (The word kinetic implies motion). The kinetic theory makes the following assumptions.

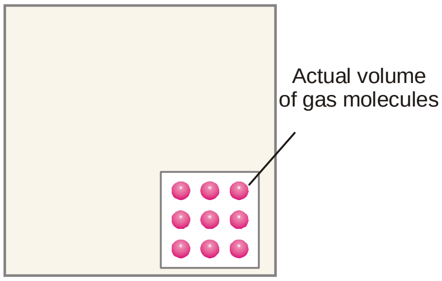
Assumptions of the Kinetic Molecular Theory

(1) **A gas consists of extremely small discrete particles called molecules dispersed throughout**

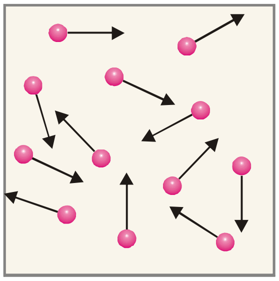
the container. The actual volume of the molecules is negligible compared to the total volume of the gas. The molecules of a given gas are identical and have the same mass (*m*).



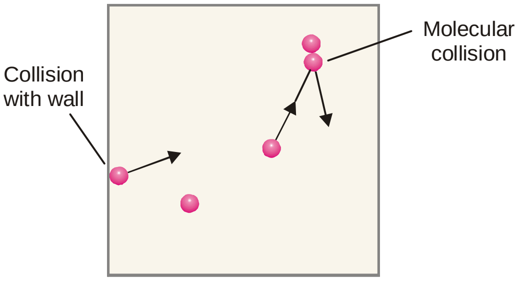
■ **Figure 10.13**
A gas is made of molecules dispersed in space in the container.



■ **Figure 10.14**
Actual volume of the gas molecules is negligible.



■ **Figure 10.15**
Gas molecules are in constant motion in all possible directions.



■ **Figure 10.16**
Molecules move in straight line and change direction on collision with another molecule or wall of container.

(2) **Gas molecules are in constant random motion with high velocities.** They move in straight lines with uniform velocity and change direction on collision with other molecules or the walls of the container. Pool table analogy is shown in Fig.10.17.

■ **Figure 10.17**
Gas molecules can be compared to billiard balls in random motion, bouncing off each other and off the sides of the pool table.

(3) The distance between the molecules are very large and it is assumed that van der Waals attractive forces between them do not exist. Thus **the gas molecules can move freely, independent of each other.**

(4) All collisions are perfectly elastic. Hence, **there is no loss of the kinetic energy of a molecule during a collision.**

(5) **The pressure of a gas is caused by the hits recorded by molecules on the walls of the container.**

(6) The average kinetic energy $\left(\frac{1}{2}mv^2\right)$ of the gas molecules is directly proportional to absolute temperature (Kelvin temperature). This implies that **the average kinetic energy of molecules is the same at a given temperature.**

How Does an Ideal Gas Differ from Real Gases ?

A gas that confirms to the assumptions of the kinetic theory of gases is called an ideal gas. It obeys the basic laws strictly under all conditions of temperature and pressure.

The **real gases** as hydrogen, oxygen, nitrogen etc., are opposed to the assumptions (1), (2) and (3) stated above. Thus :

(*a*) The actual volume of molecules in an ideal gas is negligible, while in a real gas it is appreciable.

(*b*) There are no attractive forces between molecules in an ideal gas while these exist in a real gas.

(*c*) Molecular collisions in an ideal gas are perfectly elastic while it is not so in a real gas.

For the reasons listed above, real gases obey the gas laws under moderate conditions of temperature and pressure. At very low temperature and very high pressure, the clauses (1), (2) and (3) of kinetic theory do not hold. Therefore, under these conditions the real gases show considerable deviations from the ideal gas behaviour.

DERIVATION OF KINETIC GAS EQUATION

Starting from the postulates of the kinetic molecular theory of gases we can develop an important equation. This equation expresses PV of a gas in terms of the number of molecules, molecular mass and molecular velocity. This equation which we shall name as the *Kinetic Gas Equation* may be derived by the following clauses.

Let us consider a certain mass of gas enclosed in a cubic box (Fig. 10.18) at a fixed temperature. Suppose that :

the length of each side of the box $= l$ cm
the total number of gas molecules $= n$
the mass of one molecule $= m$
the velocity of a molecule $= v$

The kinetic gas equation may be derived by the following steps :

(1) Resolution of Velocity *v* of a Single Molecule Along *X*, *Y* and *Z* Axes

According to the kinetic theory, a molecule of a gas can move with velocity v in any direction. Velocity is a vector quantity and can be resolved into the components v_x, v_y, v_z along the X, Y and Z axes. These components are related to the velocity v by the following expression.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Now we can consider the motion of a single molecule moving with the component velocities independently in each direction.

(2) The Number of Collisions Per Second on Face A Due to One Molecule

Consider a molecule moving in *OX* direction between opposite faces *A* and *B*. It will strike the face *A* with velocity v_x and rebound with velocity $-v_x$. To hit the same face again, the molecule must travel *l* cm to collide with the opposite face *B* and then again *l* cm to return to face *A*. Therefore,

the time between two collisions of face $A_v = \dfrac{2l}{v_x}$ seconds

the number of collisions per second on face $A = \dfrac{v_x}{2l}$

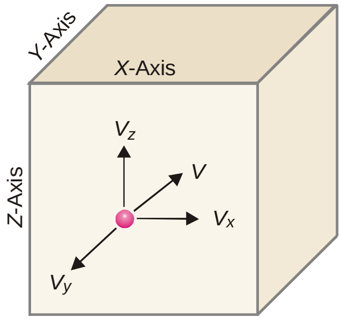


Figure 10.18
Resolution of velocity v into components V_x, V_y and V_z.

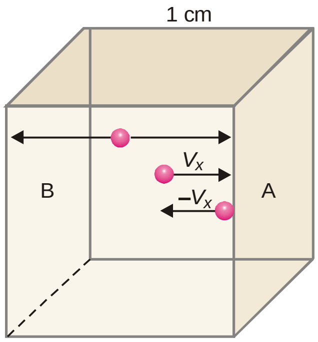


Figure 10.19
Cubic box showing molecular collisions along *X* axis.

(3) The Total Change of Momentum on All Faces of the Box Due to One Molecule Only

Each impact of the molecule on the face *A* causes a change of momentum (mass × velocity) :

the momentum before the impact $= mv_x$

the momentum after the impact $= m(-v_x)$

∴ the change of momentum $= mv_x - (-mv_x)$

$= 2\,mv_x$

But the number of collisions per second on face *A* due to one molecule $= \dfrac{v_x}{2l}$

Therefore, the total change of momentum per second on face *A* caused by one molecule

$$= 2m\,v_x \times \left(\frac{v_x}{2l}\right) = \frac{m\,v_x^2}{l}$$

The change of momentum on both the opposite faces *A* and *B* along *X*-axis would be double *i.e.*, $2mv_x^2/l$ similarly, the change of momentum along *Y*-axis and *Z*-axis will be $2mv_y^2/l$ and $2mv_z^2/l$ respectively. Hence, the overall change of momentum per second on all faces of the box will be

$$= \frac{2mv_x^2}{l} + \frac{2mv_y^2}{l} + \frac{2mv_z^2}{l}$$

$$= \frac{2m}{l}(v_x^2 + v_y^2 + v_z^2)$$

$$= \frac{2m\,v^2}{l} \qquad (\quad v^2 = v_x^2 + v_y^2 + v_z^2)$$

(4) Total Change of Momentum Due to Impacts of All the Molecules on All Faces of the Box

Suppose there are N molecules in the box each of which is moving with a different velocity v_1, v_2, v_3, etc. The total change of momentum due to impacts of all the molecules on all faces of the box

$$= \frac{2m}{l}(v_1^2 + v_2^2 + v_3^2 + ...)$$

Multiplying and dividing by n, we have

$$= \frac{2mN}{l}\left(\frac{v_1^2 + v_2^2 + v_3^2 + ...}{n}\right)$$

$$= \frac{2mN\ u^2}{l}$$

where u^2 is the **mean square velocity.**

(5) Calculation of Pressure from Change of Momentum; Derivation of Kinetic Gas Equation

Since force may be defined as the change in momentum per second, we can write

$$\text{Force} = \frac{2mN\ u^2}{l}$$

But

$$\text{Pressure} = \frac{\text{Total Force}}{\text{Total Area}}$$

$$P = \frac{2mNu^2}{l} \times \frac{1}{6l^2} = \frac{1}{3}\frac{mNu^2}{l^3}$$

Since l^3 is the volume of the cube, V, we have

$$P = \frac{1}{3}\frac{mNu^2}{V}$$

or

$$P\ V = \frac{1}{3}mNu^2$$

This is the fundamental equation of the kinetic molecular theory of gases. It is called the **Kinetic Gas equation.** This equation although derived for a cubical vessel, is equally valid for a vessel of any shape. The available volume in the vessel could well be considered as made up of a large number of infinitesimally small cubes for each of which the equation holds.

Significance of the term *u*. As stated in clause (4) u^2 is the mean of the squares of the individual velocities of all the N molecules of the gas. But $u = \sqrt{u^2}$. Therefore u is called the **Root Mean Square (or RMS) Velocity.**

KINETIC GAS EQUATION IN TERMS OF KINETIC ENERGY

If N be the number of molecules in a given mass of gas,

$$P\ V = \frac{1}{3}mNu^2 \qquad \text{(Kinetic Gas equation)}$$

$$= \frac{2}{3}N \times \frac{1}{2}mu^2$$

$$= \frac{2}{3}N \times e$$

where e is the average kinetic energy of a single molecule.

$$\therefore \qquad PV = \frac{2}{3}Ne = \frac{2}{3}E$$

or $$PV = \frac{2}{3}E \qquad ...(1)$$

where E is the total kinetic energy of all the N molecules. The expression (1) may be called the kinetic gas equation in terms of kinetic energy.

We know that the General ideal gas equation is

$$PV = nRT \qquad ...(2)$$

From (1) and (2)

$$\frac{2}{3}E = nRT \qquad ...(3)$$

For one mole of gas, the kinetic energy of N molecules is,

$$E = \frac{3RT}{2} \qquad ...(4)$$

Since the number of gas molecules in one mole of gas in N_0 (Avogadro number),

$$e = \frac{E}{N_0} = \frac{3RT}{2N_0}$$

or $$e = \frac{3RT}{2N_0} \qquad ...(5)$$

substituting the values of R, T, N_0, in the equation (5), the average kinetic energy of a gas molecule can be calculated.

SOLVED PROBLEM 1. Calculate the average kinetic energy of a hydrogen molecule at 0°C.

SOLUTION

$$e = \frac{3RT}{2N_0}$$

Here $R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$

$T = 273 \text{ K}$; $N_0 = 6.02 \times 10^{23}$

$$\therefore \quad e = \frac{3}{2} \times \frac{8.314 \times 10^7 \times 273}{6.02 \times 10^{23}} = \mathbf{5.66 \times 10^{-14} \text{ erg}}$$

Thus the average kinetic energy of H_2 at 0°C is **5.66×10^{-14} erg**

SOLVED PROBLEM 2. Calculate the kinetic energy of two moles of N_2 at 27°C. ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

SOLUTION

We know $$E = \frac{3}{2}nRT$$

Here, $T = 27 + 273 = 300 \text{ K}$; $n = 2$; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

Substituting these values, we have

$$E = \frac{3}{2} \times 2 \times 8.314 \times 300 = \mathbf{7482.6 \text{ J}}$$

Therefore the kinetic energy of two moles of N_2 is **7482.6 J.**

DEDUCTION OF GAS LAWS FROM THE KINETIC GAS EQUATION

(*a*) Boyle's Law

According to the Kinetic Theory, there is a direct proportionality between absolute temperature and average kinetic energy of the molecules *i.e.*,

$$\frac{1}{2}mNu^2 \propto T$$

or $$\frac{1}{2}mNu^2 = kT$$

or $$\frac{3}{2}\times\frac{1}{3}mNu^2 = kT$$

or $$\frac{1}{3}mNu^2 = \frac{2}{3}kT$$

Substituting the above value in the kinetic gas equation $PV = \frac{1}{3}mNu^2$, we have

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

The product PV, therefore, will have a constant value at a constant temperature. This is Boyle's Law.

(*b*) Charles' Law

As derived above,

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

or $$V = \frac{2}{3}\times\frac{k}{P}T$$

At constant pressure,

$$V = k'\,T \qquad \text{where } \left(k' = \frac{2}{3}\times\frac{k}{P}\right)$$

or $$V \propto T$$

That is, at constant pressure, volume of a gas is proportional to Kelvin temperature and this is Charles' Law.

(*c*) Avogadro's Law

If equal volume of two gases be considered at the same pressure,

$$PV = \frac{1}{3}m_1N_1u_1^2 \qquad \text{...Kinetic equation as applied to one gas}$$

$$PV = \frac{1}{3}m_2N_2u_2^2 \qquad \text{...Kinetic equation as applied to 2nd gas}$$

$$\therefore \quad \frac{1}{3}m_1N_1u_1^2 = \frac{1}{3}m_2N_2u_2^2 \qquad \text{...(1)}$$

When the temperature (T) of both the gases is the same, their mean kinetic energy per molecule will also be the same.

i.e., $$\frac{1}{3}m_1u_1^2 = \frac{1}{3}m_2u_2^2 \qquad \text{...(2)}$$

Dividing (1) by (2), we have

DEDUCTION OF GAS LAWS FROM THE KINETIC GAS EQUATION

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When the temperature (*T*) of both the gases is the same, their mean kinetic energy per molecule will also be the same.

i.e., $$\frac{1}{3}m_1u_1^2 = \frac{1}{3}m_2u_2^2 \qquad \text{...(2)}$$

Dividing (1) by (2), we have

$$N_1 = N_2$$

Or, under the same conditions of temperature and pressure, equal volumes of the two gases contain the same number of molecules. This is Avogadro's Law.

(*d*) Graham's Law of Diffusion

If m_1 and m_2 are the masses and u_1 and u_2 the velocities of the molecules of gases 1 and 2, then at the same pressure and volume

$$\frac{1}{3} m_1 N_1 u_1^2 = \frac{1}{3} m_2 N_2 u_2^2$$

By Avogadro's Law $\qquad N_1 = N_2$

$\therefore \qquad m_1 u_1^2 = m_2 u_2^2$

or $\qquad \left(\frac{u_1}{u_2}\right)^2 = \frac{m_2}{m_1}$

If M_1 and M_2 represent the molecular masses of gases 1 and 2,

$$\left(\frac{u_1}{u_2}\right)^2 = \frac{M_2}{M_1}$$

$$\frac{u_1}{u_2} = \sqrt{\frac{M_2}{M_1}}$$

The rate of diffusion (r) is proportional to the velocity of molecules (u), Therefore,

$$\frac{\text{Rate of diffusion of gas 1}}{\text{Rate of diffusion of gas 2}} = \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

This is Graham's Law of Diffusion.

DISTRIBUTION OF MOLECULAR VELOCITIES

While deriving Kinetic Gas Equation, it was assumed that all molecules in a gas have the same velocity. But it is not so. When any two molecules collide, one molecule transfers kinetic energy ($\frac{1}{2} mv^2$) to the other molecule. The velocity of the molecule which gains energy increases and that of the other decreases. Millions of such molecular collisions are taking place per second. Therefore, the velocities of molecules are changing constantly. Since the number of molecules is very large, a fraction of molecules will have the same particular velocity. In this way there is a broad distribution of velocities over different fractions of molecules. In 1860 James Clark Maxwell calculated the distribution of velocities from the laws of probability. He derived the following equation for the distribution of molecular velocities.

$$\frac{dN_c}{N} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} e^{\frac{-MC^2}{2RT}} C^2\, dc$$

where $\quad dN_c$ = number of molecules having velocities between C and $(C + dc)$

N = total number of molecules

M = molecular mass

T = temperature on absolute scale (K)

The relation stated above is called **Maxwell's law of distribution of velocities.** The ratio dn_c/n gives the fraction of the total number of molecules having velocities between C and $(C + dc)$. Maxwell plotted such fractions against velocity possessed by the molecules. The curves so obtained illustrate the salient features of Maxwell distribution of velocities.

Fig. 10.20. Shows the distribution of velocities in nitrogen gas, N_2, at 300 K and 600 K. It will be noticed that :

(1) A very small fraction of molecules has either very low (close to zero) or very high velocities.

(2) Most intermediate fractions of molecules have velocities close to an average velocity represented by the peak of the curve. This velocity is called the **most probable velocity.** It may be defined as the velocity possessed by the largest fraction of molecules corresponding to the highest point on the Maxwellian curve.

(3) At higher temperature, the whole curve shifts to the right (dotted curve at 600 K). This shows that **at higher temperature more molecules have higher velocities and fewer molecules have lower velocities.**

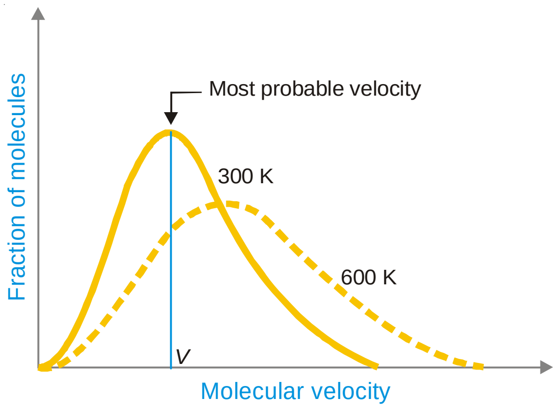

Figure 10.20

Distribution of molecular velocities in nitrogen gas, N_2, at 300 K and 600 K.

DIFFERENT KINDS OF VELOCITIES

In our study of kinetic theory we come across three different kinds of molecular velocities :

(1) the Average velocity (V)

(2) the Root Mean Square velocity (μ)

(3) the Most Probable velocity (v_{mn})

Average Velocity

Let there be n molecules of a gas having individual velocities v_1, v_2, v_3 ..... v_n. The ordinary average velocity is the arithmetic mean of the various velocities of the molecules.

$$\bar{v} = \frac{v_1 + v_2 + v_3 \text{ ..... } + v_n}{n}$$

From Maxwell equation it has been established that the average velocity v_{av} is given by the expression

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

Substituting the values of R, T, π and M in this expression, the average value can be calculated.

Root Mean Square Velocity

If v_1, v_2, v_3 ..... v_n are the velocities of n molecules in a gas, μ^2, the mean of the squares of all the velocities is

$$\mu^2 = \frac{v_1^2 + v_2^2 + v_3^2 \; ..... + v_n^2}{n}$$

Taking the root

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 \; ..... + v_n^2}{n}}$$

μ is thus the **Root Mean Square velocity or RMS velocity.** It is denoted by *u*.

The value of the RMS of velocity *u*, at a given temperature can be calculated from the Kinetic Gas Equation.

$$PV = \frac{1}{3} mNu^2 \qquad \text{...Kinetic Equation}$$

$$u^2 = \frac{3PV}{mN}$$

For one mole of gas

$$PV = RT$$

Therefore,

$$u^2 = \frac{3RT}{M} \qquad \text{...}M \text{ is molar mass}$$

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

By substituting the values of *R*, *T* and *M*, the value of *u* (RMS velocity) can be determined.

RMS velocity is superior to the average velocity considered earlier. With the help of *u*, the total Kinetic energy of a gas sample can be calculated.

Most Probable Velocity

As already stated the most probable velocity is possessed by the largest number of molecules in a gas. According to the calculations made by Maxwell, the most probably velocity, v_{mp}, is given by the expression.

$$v_{mps} \quad \sqrt{\frac{2RT}{M}}$$

Substituting the values of *R*, *T* and *M* in this expression, the most probably velocity can be calculated.

Relation between Average Velocity, RMS Velocity and Most Probable Velocity

We know that the average velocity, $\bar{v}$, is given by the expression

$$\bar{v} = \sqrt{\frac{8RT}{\pi M}}$$

and

$$\mu = \sqrt{\frac{3RT}{M}}$$

∴

$$\frac{\bar{v}}{\mu} = \sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}}$$

$$= 0.9213$$

or

$$\bar{v} = \mu \times 0.9213 \qquad \text{...(1)}$$

That is, **Average Velocity = 0.9213 × RMS Velocity**

The expression for the most probably velocity, v_{mp}, is

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

and
$$\mu = \sqrt{\frac{3RT}{M}}$$

∴
$$\frac{v_{mp}}{\mu} = \sqrt{\frac{2RT}{M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{2}{3}} = 0.8165$$

or
$$v_{mp} = \mu \times 0.8165 \qquad ...(2)$$

That is, **Most Probable Velocity = 0.8165 × RMS Velocity**

RMS can be easily calculated by the application of Kinetic Gas equation. Knowing the value of RMS, we can find the average velocity and the most probable velocity from expressions (1) and (2).

CALCULATION OF MOLECULAR VELOCITIES

The velocities of gas molecules are exceptionally high. Thus velocity of hydrogen molecule is 1,838 metres sec^{-1}. While it may appear impossible to measure so high velocities, these can be easily calculated from the Kinetic Gas equation. Several cases may arise according to the available data.

While calculating different types of velocities, we can also make use of the following expressions stated already.

RMS velocity,
$$\mu = \sqrt{\frac{3RT}{M}}$$

Average velocity,
$$\bar{v} = \sqrt{\frac{8RT}{M}}$$

Most Probable velocity,
$$v_{mp} = \sqrt{\frac{2RT}{M}}$$

Case 1. Calculation of Molecular Velocity when temperature alone is given

$$PV = \frac{1}{3} mNu^2 \qquad \text{(Kinetic Gas equation)}$$

where
$$N = N_0 \qquad \text{(Avogadro's number)}$$

Thus we have,

$$M = m \times N_0 = \text{molecular mass of the gas}$$

∴
$$u = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}} \qquad (\because\ PV = RT \text{ for 1 mole})$$

But
$$R = 8.314 \times 10^7 \text{ ergs deg}^{-1}\text{ mol}^{-1}$$
$$= 0.8314 \times 10^8 \text{ ergs deg}^{-1}\text{ mol}^{-1}$$

∴
$$u = \sqrt{\frac{3 \times 0.8314 \times 10^8 \times T}{M}}$$

$$= \mathbf{1.58 \times 10^4 \times \sqrt{\frac{T}{M}}\ \text{cm sec}^{-1}}$$

where T is Kelvin temperature and M the molar mass.

SOLVED PROBLEM. Calculate the root mean square velocity of CO_2 molecule at 1000°C.

SOLUTION

$$T = 273 + 1000 = 1273\text{ K};\ M = 44$$

Applying the equation

$$u = 1.58 \times 10^4 \times \sqrt{\frac{T}{M}}$$

we have

$$u = 1.58 \times 10^4 \times \sqrt{\frac{1273}{44}}$$

$$\mathbf{u = 84985\ cm\ \ sec^{-1}\ \ or\ \ \ 849.85\ m\ \ sec^{-1}}$$

Case 2. Calculation of Molecular Velocity when temperature and pressure both are given.

In such cases we make use of the following relation based on Kinetic Gas equation.

$$u = \sqrt{\frac{3PV}{M}}$$

We know that 1 mole of a gas at STP occupies a volume of 22400 ml (known as molar volume). But before applying this relation the molar volume is reduced to the given conditions of temperature and pressure.

SOLVED PROBLEM. Calculate the RMS velocity of chlorine molecules at 12°C and 78 cm pressure.

SOLUTION

At STP :	At given conditions :
$V_1 = 22400$ ml	$V_2 = ?$
$T_1 = 273$ K	$T_2 = 12 + 273 = 285$ K
$P_1 = 76$ cm	$P_2 = 78$ cm

Applying

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

we have

$$V_2 = \frac{P_1\ V_1\ T_2}{T_1\ P_2} = \frac{76 \times 22400 \times 285}{273 \times 78} = 22785\text{ ml}$$

we know that

$$u = \sqrt{\frac{3PV}{M}}$$

$$P = hdg = 78 \times 13.6 \times 981\text{ dynes cm}^{-2}$$

$$V = 22785\text{ ml};\ M = 71$$

∴

$$u = \sqrt{\frac{3 \times 78 \times 13.6 \times 981 \times 22785}{71}}$$

$$\mathbf{u = 31652\ cm\ sec^{-1}\ \ or\ \ 316.52\ m\ sec^{-1}}$$

Case 3. Calculation of Molecular Velocity at STP

Here we use the relation

$$u = \sqrt{\frac{3PV}{M}}$$

where $P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$

$V = 22{,}400 \text{ ml}$

$M = \text{Molar mass of the gas}$

SOLVED PROBLEM. Calculate the average velocity of nitrogen molecule at STP.

SOLUTION

In this example we have,

$P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$

$V = 22{,}400 \text{ ml}$

$M = 28$

Substituting these values in the equation

$$u = \sqrt{\frac{3PV}{M}}$$

we have

$$= \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{28}}$$

$$= 49{,}330 \text{ cm sec}^{-1}$$

$$\therefore \text{ Average velocity } = 0.9213 \times 49330 \text{ cm sec}^{-1}$$

$$= \mathbf{45{,}447 \text{ cm sec}^{-1}}$$

Case 4. Calculation of Molecular Velocity when pressure and density are given

In this case we have

$$u = \sqrt{\frac{3PV}{M}} \quad \text{or} \quad u = \sqrt{\frac{3P}{D}} \qquad \left[\frac{M}{V} = D\right]$$

where P is expressed in dynes cm^{-2} and D in gm ml^{-1}.

SOLVED PROBLEM. Oxygen at 1 atmosphere pressure and 0°C has a density of 1.4290 grams per litre. Find the RMS velocity of oxygen molecules.

SOLUTION

We have $P = 1 \text{ atm} = 76 \times 13.6 \times 981 \text{ dynes cm}^{-2}$

$$D = 1.4290 \text{ g } l^{-1} = \frac{1.4290}{1000} \text{ g ml}^{-1}$$

$$= 0.001429 \text{ g ml}^{-1}$$

Applying

$$u = \sqrt{\frac{3P}{D}}$$

we get

$$u = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}} = \mathbf{46138 \text{ cm sec}^{-1}}$$

Case 5. Calculation of most probable velocity

In this case we have

$$v_{mp} = 1.29 \times 10^4 \sqrt{\frac{T}{M}}$$

where T expressed in Kelvin and M to mass.

SOLVED PROBLEM. Calculate the most probable velocity of nitrogen molecules, N_2, at 15°C.

SOLUTION

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

We know that

$$v_{mp} = 1.29 \times 10^4 \sqrt{\frac{T}{M}}$$

$$= 1.29 \times 10^4 \sqrt{\frac{288}{28}}$$

$$= \mathbf{4.137 \times 10^4 \text{ cm sec}^{-1}}$$

COLLISION PROPERTIES

In the derivation of Kinetic gas equation we did not take into account collisions between molecules. The molecules in a gas are constantly colliding with one another. The transport properties of gases such as diffusion, viscosity and mean free path depend on molecular collisions. We will now discuss some properties of gases which determine the frequency of collisions.

The Mean Free Path

At a given temperature, a molecule travels in a straight line before collision with another molecule. The distance travelled by the molecule before collision is termed *free path*. The free path for a molecule varies from time to time. **The mean distance travelled by a molecule between two successive collisions is called the Mean Free Path.** It is denoted by λ. If l_1, l_2, l_3 are the free paths for a molecule of a gas, its free path

$$\lambda = \frac{l_1 + l_2 + l_3 + ... + l_n}{n}$$

where n is the number of molecules with which the molecule collides. Evidently, the number of molecular collisions will be less at a lower pressure or lower density and longer will be the mean free path. The mean free path is also related with the viscosity of the gas.

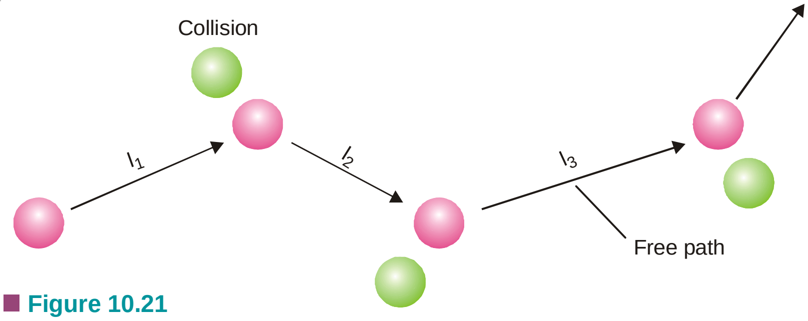

Figure 10.21
The mean free path illustrated.

The mean free path, λ, is given by the expression

$$\lambda = \eta\sqrt{\frac{3}{Pd}}$$

where
P = pressure of the gas
d = density of the gas
η = coefficient of viscosity of the gas

By a determination of the viscosity of the gas, the mean free path can be readily calculated. At STP, the mean free path for hydrogen is 1.78×10^{-5} cm and for oxygen it is 1.0×10^{-5} cm.

Effect of Temperature and Pressure on Mean Free Path

(*a*) Temperature

The ideal gas equation for *n* moles of a gas is

$$PV = n R T \qquad ...(i)$$

where *n* is the number of moles given by

$$n = \frac{\text{Number of molecules}}{\text{Avogadro's Number}} = \frac{N}{N_0}$$

Substituting this in equation (*i*) we get

$$PV = \frac{N}{N_o} RT$$

or

$$\frac{N}{V} = \frac{PN_0}{RT}$$

At constant pressure

$$N \propto \frac{1}{T} \qquad ...(ii)$$

The mean free path is given by

$$\lambda = \frac{\text{Distance travelled by the molecule per second}}{\text{Number of collisions per c.c.}}$$

$$= \frac{\bar{v}}{\sqrt{2}\ \pi\sigma^2 \bar{v}\bar{N}}$$

$$= \frac{1}{\sqrt{2}\ \pi\sigma^2 \bar{N}} \qquad ...(iii)$$

combining equations (*ii*) and (*iii*), we get

$$\lambda \propto T$$

Thus, *the mean free path is directly proportional to the absolute temperature*.

(*b*) Pressure

We know that the pressure of a gas at certain temperature is directly proportional to the number of molecules per c.c. *i.e.*

$$P \propto \bar{N}$$

and mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \bar{N}}$$

Combining these two equations, we get

$$\lambda \propto \frac{1}{P}$$

Thus, **the mean free path of a gas is directly proportional to the pressure of a gas at constant temperature.**

SOLVED PROBLEM 1. At 0°C and 1 atmospheric pressure the molecular diameter of a gas is 4Å. Calculate the mean free path of its molecule.

SOLUTION. The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2 \bar{N}}$$

where σ is the molecular diameter

and $\bar{N}$ is the no. of molecules per c.c.

Here $\sigma = 4\text{Å} = 4 \times 10^{-8}$ cm.

We know 22400 ml of a gas 0°C and 1 atm. pressure contains 6.02×10^{23} molecules.

$$\therefore \quad \text{No. of molecules per c.c., } \bar{N} = \frac{6.02 \times 10^{23}}{22400}$$

$$= 2.689 \times 10^{19} \text{ molecules}$$

Substituting the values, we get

$$\sigma = \frac{1}{1.414 \times 3.14 \times (4 \times 10^{-8})^2 \times 2.689 \times 10^{19}}$$

$$= \frac{1}{1.414 \times 3.14 \times 16 \times 2.689 \times 10^{3}}$$

$$= \mathbf{0.524 \times 10^{-5}\ cm}$$

SOLVED PROBLEM 2. The root mean square velocity of hydrogen at STP is 1.83×10^5 cm sec^{-1} and its mean free path is 1.78×10^{-5} cm. Calculate the collision number at STP.

SOLUTION. Here root mean square velocity

$$\mu = 1.831 \times 10^5 \text{ cm sec}^{-1}$$

We know average velocity $\bar{v} = 0.9213 \times \text{RMS velocity}$

$$= 0.9213 \times 1.831 \times 10^5 \text{ cm sec}^{-1}$$

$$= 1.6869 \times 10^5 \text{ cm sec}^{-1}$$

$$\text{The mean free path} = \frac{\text{Average velocity}}{\text{Collision Number}}$$

$$\therefore \quad \text{Collision Number} = \frac{\text{Average velocity}}{\text{Mean free path}}$$

$$= \frac{1.6869 \times 10^5 \text{ cm sec}^{-1}}{1.78 \times 10^{-5} \text{ cm.}}$$

$$= \mathbf{9.4769 \times 10^9\ sec^{-1}}$$

The Collison Diameter

When two gas molecules approach one another, they cannot come closer beyond a certain distance. **The closest distance between the centres of the two molecules taking part in a collision is called the Collision Diameter.** It is denoted by σ. Whenever the distance between the centres of two molecules is σ, a collison occurs.

The collision diameter is obviously related to the mean free path of molecules. **The smaller the collision or molecular diameter, the larger is the mean free path.**

SOLVED PROBLEM 1. At 0°C and 1 atmospheric pressure the molecular diameter of a gas is 4Å. Calculate the mean free path of its molecule.

SOLUTION. The mean free path is given by

$$\lambda = \frac{1}{\sqrt{2}\,\pi\sigma^2\bar{N}}$$

where σ is the molecular diameter

and $\bar{N}$ is the no. of molecules per c.c.

Here $\sigma = 4\text{Å} = 4 \times 10^{-8}$ cm.

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$$\text{The mean free path} = \frac{\text{Average velocity}}{\text{Collision Number}}$$

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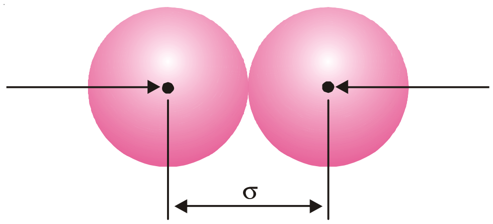

Figure 10.22
Collision diameter of molecules.

The collision diameter can be determined from viscosity measurements. The collision diameter of hydrogen is 2.74 Å and that of oxygen is 3.61Å.

The Collision Frequency

The collision frequency of a gas is defined as :

the number of molecular collisions taking place per second per unit volume (c.c.) of the gas.

Let a gas contain $\bar{N}$ molecules per c.c. From kinetic consideration it has been established that the number of molecules, *n*, with which a single molecule will collide per second, is given by the relation

$$n = \sqrt{2}\, \pi\, \bar{v}\, \sigma^2\, N$$

where $\bar{v}$ = average velocity; σ= collision diameter.

If the total number of collisions taking place per second is denoted by Z, we have

$$Z = \sqrt{2}\, \pi\, \bar{v}\, \sigma^2\, N \times N$$
$$= \sqrt{2}\, \pi\, \bar{v}\, \sigma^2\, N^2$$

Since each collision involves two molecules, the number of collision per second per c.c. of the gas will be *Z*/2.

$$\text{Hence the collision frequency } = \frac{\sqrt{2}\,\pi\bar{v}\,\sigma^2\,N^2}{2}$$
$$= \frac{\pi\bar{v}\,\sigma^2\,N^2}{\sqrt{2}}$$

Evidently, **the collision frequency of a gas increases with increase in temperature, molecular size and the number of molecules per c.c.**

Effect of Temperature and Pressure on Collision Frequency

(i) Effect of Temperature

We know collision frequency is given by

$$Z = \frac{\pi\bar{v}\,\sigma^2\,\bar{N}^2}{\sqrt{2}} \qquad \ldots(i)$$

From this equation it is clear that

$$Z \propto \bar{v}$$

But $\mu \propto \sqrt{T}$

or $Z \propto \sqrt{T}$

Hence collision frequency is directly proportional to the square root of absolute temperature.

(*ii*) Effect of Pressure

From equation (*i*), we have

$$Z \propto \bar{N}^2 \qquad \text{...}(ii)$$

where $\bar{N}$ is the number of molecules per c.c. But we know that the pressure of the gas at a certain temperature *i.e.*

$$P \propto \bar{N} \qquad \text{...}(iii)$$

combining equation (*ii*) and (*iii*) we get

$$Z = P^2$$

Thus the collision frequency is directly proportional to the square of the pressure of the gas.

SPECIFIC HEAT RATIO OF GASES

The Specific heat is defined as the amount of heat required to raise the temperature of one gram of a substance through 1°C. It may be measured at constant volume or at a constant pressure and though the difference in the two values is negligible in case of solids and liquids, it is appreciable in case of gases and a ratio of the two values gives us valuable information about the atomicity of a gas molecule.

Specific Heat at Constant Volume

It is the amount of heat required to raise the temperature of one gas through 1°C while the volume is kept constant and the pressure allowed to increase. It is denoted by the symbol C_v. In Physical Chemistry it is more common, however, to deal with one gram mole of the gas and the heat required in such case is called **Molecular Heat** and is represented at constant volume by C_v.

It is possible to calculate its value by making use of the Kinetic theory.

Consider one mole of a gas at the temperature T. Its kinetic energy is $\frac{1}{2}mnu^2$. From the kinetic gas equation

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

$$= \frac{2}{3} \times \frac{1}{2}mnu^2 = RT$$

or

$$\frac{1}{2}mnu^2 \text{ (= KE)} = \frac{3}{2}RT$$

If the temperature is raised by 1°C to $(T + 1)K$ kinetic energy becomes $\frac{3}{2}R\,(T + 1)$.

$$\therefore \quad \text{Increase in kinetic energy} = \frac{3}{2}R\,(T + 1) - \frac{3}{2}RT$$

$$= \frac{3}{2}R$$

If, therefore, it be assumed that the heat supplied to a gas at constant volume is used up entirely in increasing the kinetic energy of the moving molecules, and consequently increasing the temperature, the value of C_v should be equal $\frac{3}{2}R$. It is actually so for monoatomic gases and vapours because such molecules can execute only translatory motion along the three co-ordinate axes. Motion of monoatomic gas molecules is the simplest and can be resolved into three perpendicular components along the co-ordinate axes. Thus the energy of such a molecule can be considered to be composed of three parts as

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

The number of square terms involved in determining the total kinetic energy of a molecule is often referred to as the **Degrees of freedom of motion.** Such molecules have three degrees of freedom of motion. According to the principle of equipartition of energy, total energy of the molecule is equally distributed among all its degrees of freedom. But in the case of diatomic and polyatomic molecules, the heat supplied may not only increase this **kinetic energy of translation** of the molecules as a whole but also cause an increase in the energy in the inside of the molecules which we may call as **intramolecular energy.** This intramolecular energy may be the **vibration energy** *i.e.*, energy of the atoms executing vibrations with respect to each other along their line of centres or **rotational energy** which manifests itself in the rotation of the molecules about axes perpendicular to the line of centres. There will be other degrees of freedom for rotational and vibrational modes of motion also. For such cases the heat needs will be complex and are denoted by '*x*' – a factor which depends upon vibrational and rotational degrees of freedom. Vibrational degrees of freedom rapidly increase with the increase in the total number of atoms in a molecule but the degrees of freedom are two for linear diatomic and three for non-linear diatomic molecules in case of rotational motion.

Consequently in such cases the molecular heat will be greater than $\frac{3}{2}R$ by the factor x.

or $$C_v = \frac{3}{2}R + x$$

The value of x varies from gas to gas and is zero for monoatomic molecules.

Specific Heat at Constant Pressure

It may be defined as the amount of heat required to raise the temperature of one gram of gas through 1°C, the pressure remaining constant while the volume is allowed to increase. It is written as c_p and the Molecular heat in this gas is represented as C_p.

Now, whenever a gas expands it has to do work against external pressure. It means that when a gas is heated under constant pressure, the heat supplied is utilised in two ways :

(1) **in increasing the kinetic energy of the moving molecules** and this has already been shown to be equal to $3/2\ R + x$ cal.

(2) **in performing external work done by the expanding gas.** The work done by the gas is equivalent to the product of the pressure and the change in volume. Let this change in volume be ΔV when the constant pressure is P and the initial volume is V.

For 1 *g* mole of the gas at temperature T,

$$PV = RT \qquad ...(i)$$

At temperature $(T + 1)\ K$

$$P(V + \Delta V) = R(T + 1) \qquad ...(ii)$$

Subtracting (*i*) from (*ii*)

$$P \times \Delta V = R$$

Hence R cal must be added to the value of $\frac{3}{2}R$ cal in order to get the thermal equivalent of the energy supplied to one gram mole of the gas in the form of heat when its temperature is raised by 1°C.

$$\therefore \qquad C_p = \frac{3}{2}R + R = \frac{5}{2}R \qquad \text{(for monoatomic molecules)}$$

For di– and polyatomic molecules, it will be $\frac{3}{2}R + x$.

Specific Heat Ratio

The ratio of the molecular heats will be the same as the ratio of the specific heats. It is represented by the symbol γ.

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + x}{\frac{3}{2}R + x}$$

For monoatomic molecules, $x = 0$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = \mathbf{1.667}$$

For diatomic molecules in most cases, $S = R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = \mathbf{1.40}$$

For polyatomic molecules, very often $x = \frac{3}{2}R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + \frac{3}{2}R}{\frac{3}{2}R + \frac{3}{2}R} = \frac{8}{6} = \mathbf{1.33}$$

These results are found to be in accord with experimental observations at 15°C given in the Table that follows and thus **specific heat ratio helps us to determine the atomicity of gas molecules.** The theoretical difference between C_p and C_v as calculated above is R and its observed value also shown in the table below comes out to about 2 calories.

Gas	C_p	C_v	$C_p–C_v = R$	g = C_p/C_v	Atomicity
Helium	5.00	3.01	1.99	1.661	1
Argon	4.97	2.98	1.90	1.667	1
Mercury vapour	6.93	4.94	1.99	1.40	2
Nitrogen	6.95	4.96	1.99	1.40	2
Oxygen	6.82	4.83	1.49	1.41	2
Carbon dioxide	8.75	6.71	2.04	1.30	3
Hydrogen sulphide	8.62	6.53	2.09	1.32	3

DEVIATIONS FROM IDEAL BEHAVIOUR

An ideal gas is one which obeys the gas laws or the gas equation $PV = RT$ at all pressures and temperatures. However no gas is ideal. Almost all gases show significant deviations from the ideal behaviour. Thus the gases H_2, N_2 and CO_2 which fail to obey the ideal-gas equation are termed **nonideal** or **real gases.**

Compressibility Factor

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the **Compressibility factor,** denoted by Z. It is defined as

$$Z = \frac{PV}{RT}$$

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

For an ideal gas, $Z = 1$ and it is independent of temperature and pressure. The deviations from ideal behaviour of a real gas will be determined by the value of Z being greater or less than 1. **The difference between unity and the value of the compressibility factor of a gas is a measure of the degree of nonideality of the gas.**

For a real gas, the deviations from ideal behaviour depend on (*i*) pressure; and temperature. This will be illustrated by examining the compressibility curves of some gases discussed below with the variation of pressure and temperature.

Effect of Pressure Variation on Deviations

Fig. 10.23 shows the compressibility factor, Z, plotted against pressure for H_2, N_2 and CO_2 at a constant temperature.

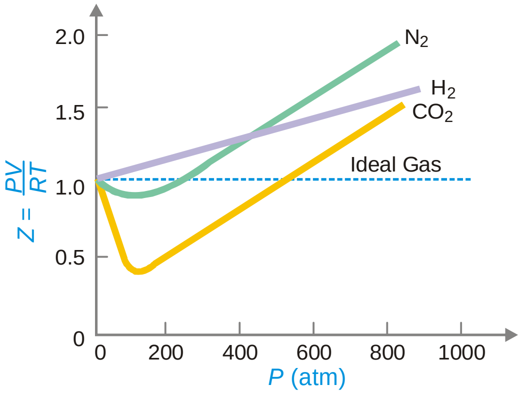

Figure 10.23

Z versus P plots for H_2, N_2 and CO_2 at 300 K.

At very low pressure, for all these gases Z is approximately equal to one. This indicates that at low pressures (upto 10 atm), real gases exhibit nearly ideal behaviour. As the pressure is increased, H_2 shows a continuous increase in Z (from $Z = 1$). Thus the H_2 curve lies above the ideal gas curve at all pressures.

For N_2 and CO_2, Z first decreases ($Z < 1$). It passes through a minimum and then increases continuously with pressure ($Z > 1$). For a gas like CO_2 the dip in the curve is greatest as it is most easily liquefied.

Effect of Temperature on Deviations

Fig 10.24 shows plots of Z or PV/RT against P for N_2 at different temperatures. It is clear from the shape of the curves that **the deviations from the ideal gas behaviour become less and less with increase of temperature.** At lower temperature, the dip in the curve is large and the slope of the curve is negative. That is, $Z < 1$. As the temperature is raised, the dip in the curve decreases. At a certain temperature, the minimum in the curve vanishes and the curve remains horizontal for an appreciable range of pressures. At this temperature, PV/RT is almost unity and the Boyle's law is obeyed. Hence this temperature for the gas is called **Boyle's temperature.** The Boyle temperature of each gas is characteristic *e.g.*, for N_2 it is 332 K.

Conclusions

From the above discussions we conclude that :

(1) **At low pressures and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.**

(2) **At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.**

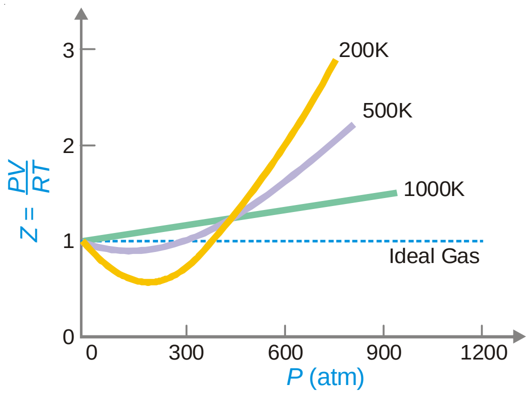

Figure 10.24
Z versus *P* plots for N_2 at different temperatures.

(3) **The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behaviour.**

EXPLANATION OF DEVIATIONS – VAN DER WAALS EQUATION

van der Waals (1873) attributed the deviations of real gases from ideal behaviour to two erroneous postulates of the kinetic theory. These are :

(1) **the molecules in a gas are point masses and possesses no volume.**

(2) **there are no intermolecular attractions in a gas.**

Therefore, the ideal gas equation $PV = nRT$ derived from kinetic theory could not hold for real gases. van der Waals pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation needed correction in order to make it applicable to real gases.

Volume Correction

The volume of a gas is the free space in the container in which molecules move about. **Volume V of an ideal gas is the same as the volume of the container.** The dot molecules of ideal gas have zero-volume and the entire space in the container is available for their movement. However, van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume.

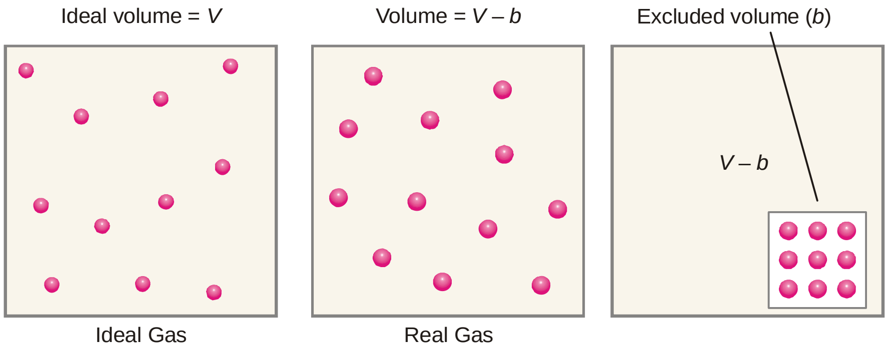

Figure 10.25
Volume of a Real gas.

The volume of a real gas is, therefore, ideal volume minus the volume occupied by gas molecules (Fig. 10.25). If b is the effective volume of molecules per mole of the gas, the volume in the ideal gas equation is corrected as :

$$(V-b)$$

For n moles of the gas, the corrected volume is :

$$(V-nb)$$

where b is termed the **excluded volume** which is constant and characteristic for each gas.

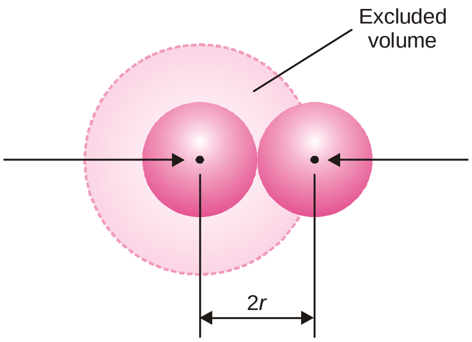

Figure 10.26

Excluded volume for a pair of gas molecules.

Excluded volume is four times the actual volume of molecules. The excluded volume is not equal to the actual volume of the gas molecules. In fact, it is four times the actual volume of molecules and can be calculated as follows.

Let us consider two molecules of radius r colliding with each other (Fig. 10.26). Obviously, they cannot approach each other closer than a distance ($2r$) apart. Therefore, the space indicated by the dotted sphere having radius ($2r$) will not be available to all other molecules of the gas. In other words the dotted spherical space is excluded volume per pair of molecules. Thus,

$$\text{excluded volume for two molecules} = \frac{4}{3}\pi(2r)^3$$

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

$$\text{excluded volume per molecule } (V_e) = \frac{1}{2}\times 8\left(\frac{4}{3}\pi r^3\right)$$

$$= 4\,V_m$$

where V_m is the actual volume of a single molecule.

Therefore, in general, excluded volume of the gas molecules is four times the actual volume of molecules.

Pressure Correction

A molecule in the interior of a gas is attracted by other molecules on all sides. These attractive forces cancel out. But a molecule about to strike the wall of the vessel is attracted by molecules on one side only. Hence it experiences an inward pull (Fig. 10.27). Therefore, it strikes the wall with reduced velocity and the actual pressure of the gas, P, will be less than the ideal pressure. If the actual pressure P, is less than P_{ideal} by a quantity p, we have

$$P = P_{\text{ideal}} - p$$

or

$$P_{\text{ideal}} = P + p$$

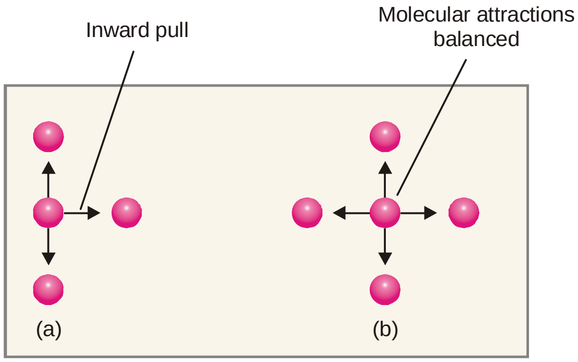

Figure 10.27

(*a*) A molecule about to strike the wall has a net inward pull;
(*b*) A molecule in the interior of gas has balanced attractions.

p is determined by the force of attraction between molecules (*A*) striking the wall of container and the molecules (*B*) pulling them inward. The net force of attraction is, therefore, proportional to the concentration of (*A*) type molecules and also of (*B*) type of molecules. That is,

$$p \propto C_A \times C_B$$

or $$p \propto \frac{n}{V} \times \frac{n}{V}$$

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

where *n* is total number of gas molecules in volume *V* and *a* is proportionality constant characteristic of the gas. Thus the pressure *P* in the ideal gas equation is corrected as :

$$\left(P + \frac{an^2}{V^2}\right)$$

for *n* moles of gas.

VAN DER WAALS EQUATION

Substituting the values of corrected pressure and volume in the ideal gas equation, $PV = nRT$, we have

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

This is known as **van der Waals equation** for *n* moles of a gas. For 1 mole of a gas ($n = 1$), van der Waals equation becomes

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

Constant *a* and *b* in van der Waals equation are called **van der Waals constants.** These constants are characteristic of each gas.

Determination of *a* and *b*

From the expression (1), the value of *a* is given by the relation

$$a = \frac{pV^2}{n^2}$$

If the pressure is expressed in atmospheres and volume in litres,

$$a = \frac{\text{(pressure) (volume)}^2}{\text{mol}^2} = \frac{\text{atm litre}^2}{\text{mol}^2}$$

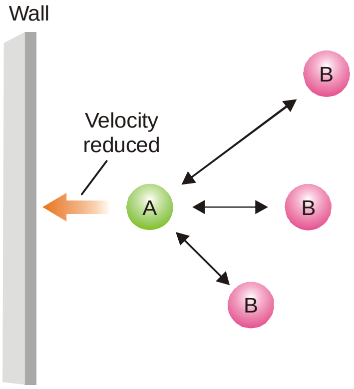

Figure 10.28

The striking molecule A is pulled inward by molecules B which reduces the velocity of A and causes the decrease of pressure.

Thus *a* is expressed in **atm litre^2 mol^{-2}** units.

Since *nb* is excluded volume for *n* moles of gas,

$$b = \frac{\text{volume}}{n} = \frac{\text{litre}}{\text{mole}}$$

If volume is expressed in litres, ***b* is expressed in litre mol^{-1}** units.

SI units of *a* and *b*. If pressure and volume are taken in SI units, we have

$$a = \frac{(\text{pressure})\ (\text{volume})}{(\text{mol})^2} = \frac{(\text{Nm}^{-2})\ (\text{m}^3)^2}{(\text{mol})^2}$$

$$= N\,\text{m}^4\,\text{mol}^{-2}$$

and

$$b = \text{Volume mol}^{-1}$$

$$= \mathbf{m^3\,mol^{-1}}$$

The values of (*a*) and (*b*) can be determined by knowing the *P*, *V* and *T* of a gaseous system under two different conditions. Table 10.2 gives values of *a* and *b* for some common gases.

TABLE 10.2. VAN DER WAALS CONSTANTS FOR SOME COMMON GASES

Gas	*a*		*b*	
	atm litre^2 mol^{-2}	N m^4 mol^{-2}	litre mol^{-1}	10^3 m^3 mol^{-1}
Hydrogen	0.245	0.0247	0.0266	0.0266
Oxygen	1.360	0.1378	0.0318	0.0318
Nitrogen	1.390	0.1408	0.0391	0.0391
Chlorine	6.493	0.6577	0.0562	0.0562
Carban dioxide	3.590	0.3637	0.0428	0.0428
Ammonia	4.170	0.4210	0.0371	0.0371
Sulphur dioxide	6.710	0.6780	0.0564	0.0564

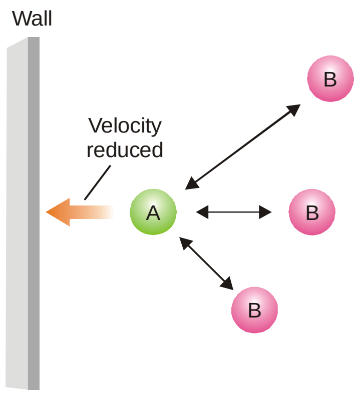

Figure 10.28

The striking molecule A is pulled inward by molecules B which reduces the velocity of A and causes the decrease of pressure.

Thus a is expressed in **atm litre^2 mol^{-2}** units.

Since nb is excluded volume for n moles of gas,

$$b = \frac{\text{volume}}{n} = \frac{\text{litre}}{\text{mole}}$$

If volume is expressed in litres, ***b* is expressed in litre mol^{-1}** units.

SI units of *a* and *b*. If pressure and volume are taken in SI units, we have

$$a = \frac{(\text{pressure})\ (\text{volume})}{(\text{mol})^2} = \frac{(\text{Nm}^{-2})\ (\text{m}^3)^2}{(\text{mol})^2}$$

$$= N\,\text{m}^4\,\text{mol}^{-2}$$

and

$$b = \text{Volume mol}^{-1}$$

$$= \mathbf{m^3\ mol^{-1}}$$

The values of (a) and (b) can be determined by knowing the P, V and T of a gaseous system under two different conditions. Table 10.2 gives values of a and b for some common gases.

TABLE 10.2. VAN DER WAALS CONSTANTS FOR SOME COMMON GASES

Gas	*a*		*b*	
	atm litre^2 mol^{-2}	N m^4 mol^{-2}	litre mol^{-1}	10^3 m^3 mol^{-1}
Hydrogen	0.245	0.0247	0.0266	0.0266
Oxygen	1.360	0.1378	0.0318	0.0318
Nitrogen	1.390	0.1408	0.0391	0.0391
Chlorine	6.493	0.6577	0.0562	0.0562
Carban dioxide	3.590	0.3637	0.0428	0.0428
Ammonia	4.170	0.4210	0.0371	0.0371
Sulphur dioxide	6.710	0.6780	0.0564	0.0564

SOLVED PROBLEM. Calculate the pressure exerted by 1.00 mole of methane (CH_4) in a 250 mL container at 300 K using van der Waals equation. What pressure will be predicted by ideal gas equation ?

$a = 2.253 \text{ L}^2 \text{ atm mol}^{-2}$, $b = 0.0428 \text{ L mol}^{-1}$; $R = 0.0821 \text{ L atm mol}^{-1} \text{ K}$.

SOLUTION

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \qquad \text{...van der Waals equation}$$

Dividing by $(V - nb)$ and solving for P

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Substituting $n = 1$, $R = 0.0821 \text{ L atm mol}^{-1} K^{-1}$, $V = 0.250$ L, $T = 300$ K and the values of a and b, we have

$$P = \frac{1 \times 0.0821 \times 300}{0.250 - (1 \times 0.0428)} - \frac{1^2 \times 2.253}{(0.250)^2}$$

$$= 82.8 \text{ atm}$$

The ideal gas equation predicts that

$$P = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{0.250}$$

$$= 98.5 \text{ atm}$$

Limitations of van der Waals Equation

van der Waals equation explains satisfactorily the general behaviour of real gases. It is valid over a wide range of pressures and temperatures. However, **it fails to give exact agreement with experimental data at very high pressures and low temperatures.** Dieterici (1899) proposed a modified van der Waals equation. This is known as **Dieterici equation.** For one mole of gas, it may be stated as

$$P(V - b) = RTe^{-a/VRT}$$

Here the terms (a) and (b) have the same significance as in van der Waals equation.

Interpretation of Deviations from van der Waals equation

For one mole of gas, van der Waals equation is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{...(1)}$$

or

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2} \qquad \text{...(2)}$$

Now we proceed to interpret the deviations of real gases from ideal behaviour as depicted in Figs. 10.21 and 10.22.

(*a*) At low pressure. When P is small, V will be large. Thus both the terms Pb and ab/V^2 in equation (2) are negligible compared to a/V. Ignoring these,

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

or

$$\frac{PV}{RT} = 1 - \frac{a}{VRT}$$

or
$$Z = 1 - \frac{a}{VRT}$$

Thus **at low pressure, the compressibility factor is less than 1.** This explains the initial portions of Z/P curves of N_2 and CO_2 which lie below the ideal curve. As the pressure is increased, V decreases and the value of Z increases. Hence the curves show upward trend.

(*b*) At high pressures. When P is large, V will be small. Therefore the terms a/V and ab/V^2 are negligible in comparison with Pb. Hence equation (2) is reduced to

$$PV = RT + Pb$$

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

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

Thus at high pressures, Z is greater than 1 and Z/P lies above the ideal gas curve. With the increase of pressure, the value of Z will be still higher. This accounts for the rising parts of the curves in Fig. 10.18.

(*c*) At extremely low pressures. At extremely low pressures, V becomes very large. Hence all the terms Pb, a/V and ab/V^2 in equation (2) are negligibly small. These could be ignored compared to RT. Thus equation (2) reduces to

$$PV = RT$$

Hence, **at low pressures real gases behave ideally.**

(*d*) At high temperatures. At high temperatures, volume will be large ($V \propto T$). Hence P will be small. Then in the equation (2) the term RT predominates the other terms and the equation is reduced to

$$PV = RT$$

Thus **at extremely high temperatures real gases tend to show ideal behaviour.**

However, at low temperatures, both P and V will be small and the net result of Pb, $-a/V$, and ab/V^2 will be appreciable. Therefore the deviations would be quite prominent.

(*e*) Exceptional behaviour of hydrogen. Because of the small mass of H_2 molecule, the attractions between the molecules are negligible. Hence the term 'a' is extremely small and the terms a/V and ab/V^2 in equation (2) can be ignored. The equation now becomes

$$PV = RT + Pb$$

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

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

Since Z is always greater than 1, **the Z/P curve throughout lies above the ideal curve.**

SOLVED PROBLEM 1. One mole of water vapour is confined to a 20 litre flask at 27°C. Calculate its pressure using

(*a*) van der Waal's equation
(*b*) Ideal gas equation

Given that
$$a = 5.464 \text{ litre}^2 \text{ atm mol}^{-1}$$
$$b = 0.0305 \text{ litre mol}^{-1}$$
$$R = 0.0821 \text{ litre atm. deg}^{-1} \text{ mol}^{-1}$$

SOLUTION. (*a*) using van der Waal's equation

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

Here $n = 1$ mole ; $T = 27 + 273 = 300$ K

$R = 0.0821$ litre atm. deg^{-1} mol^{-1}; a = 5.464 litre^2 atm. mol^{-1} and b = 0.0305 litre mol^{-1}; P = ? V = 20 litre. Substituting the values, we get

$$\left[P + \frac{5.464 \times 1^2}{(20)^2}\right][20 - 1 \times 0.0305] = 1 \times 0.0821 \times 300$$

$$[P + 0.01366]\,[19.9695] = 24.6$$

or
$$P = \frac{24.6}{19.9695} - 0.01366$$
$$= 1.23187 - 0.01366 = \mathbf{1.21821\ atm}$$

(*b*) using van der Waal's equation

$$PV = n\,RT$$

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

Substituting the values, we get

$$P = \frac{1}{20} \times 0.0821 \times 300 = \mathbf{1.2315\ atm}$$

SOLVED PROBLEM 2. Two moles of NH_3 are enclosed in a five litre flask at 27°C. Calculate the pressure exerted by the gas assuming that

(*i*) the gas behaves like an ideal gas.
(*ii*) the gas behaves like a real gas

SOLUTION. Here

$$n = 2\,;\ T = 300\ K\,;\ V = 5\ \text{litres}$$
$$R = 0.082\ \text{atm. litre K}^{-1}\ \text{mol}^{-1}$$

(*i*) when the gas behaves like an ideal gas

$$PV = n\,RT \ \text{ or } \ P = \frac{n}{V}RT$$

Substituting the values

$$P = \frac{2 \times 0.082 \times 300}{5} = \mathbf{9.84\ atm}$$

(*ii*) when the gas behaves like a real gas

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

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

Substituting the values we get

$$P = \frac{2 \times 0.082 \times 300}{5 - 2 \times 0.037} - \frac{4.14 \times 2^2}{5^2}$$
$$= 9.9879 - 0.667 = \mathbf{9.3028\ atm}$$

LIQUEFACTION OF GASES – CRITICAL PHENOMENON

A gas can be liquefied by lowering the temperature and increasing the pressure. At lower temperature, the gas molecules lose kinetic energy. The slow moving molecules then aggregate due to attractions between them and are converted into liquid. The same effect is produced by the increase of pressure. The gas molecules come closer by compression and coalesce to form the liquid.

Andres (1869) studied the $P - T$ conditions of liquefaction of several gases. He established that for every gas there is a temperature below which the gas can be liquefied but above it the gas defies liquefaction. This temperature is called the critical temperature of the gas.

The **critical temperature,** T_c, of a gas may be defined as that temperature above which it cannot be liquefied no matter how great the pressure applied.

The **critical pressure,** P_c , is the minimum pressure required to liquefy the gas at its critical temperature.

The **critical volume,** V_c, is the volume occupied by a mole of the gas at the critical temperature and critical pressure.

Tc, *Pc* and *Vc* are collectively called the **critical constants** of the gas. All real gases have characteristic critical constants.

TABLE 10.4. THE CRITICAL CONSTANTS OF SOME COMMON GASES

Gas	Critical temperature (*K*)	Critical pressure (*atm*)	Critical volume (*ml*/*mole*)
Helium	5.3	2.26	57.8
Hydrogen	33.2	12.8	65.0
Nitrogen	126.0	33.5	90.1
Oxygen	154.3	50.1	74.4
Carbon dioxide	304.0	72.9	94.0
Ammonia	405.5	111.5	72.1
Chlorine	407.1	76.1	123.8
Sulphur dioxide	430.3	77.7	122.3

At critical temperature and critical pressure, the gas becomes identical with its liquid and is said to be in **critical state.** The smooth merging of the gas with its liquid is referred to as the **critical phenomenon.** Andrews demonstrated the critical phenomenon in gases by taking example of carbon dioxide.

Andrews Isotherms of Carbon Dioxide

The *P-V* curves of a gas at constant temperature are called **isotherms** or **isothermals.** For an ideal gas $PV = nRT$ and the product PV is constant if T is fixed. Hence the isotherms would be rectangular parabolas.

For an ideal gas $PV = nRT$ and the product PV is constant if π is fixed. Hence the isotherms would be rectangular parabolas.

Andrews plotted the isotherms of carbon dioxide for a series of temperatures. From Fig. 10.30 can be seen that there are three types of isotherms *viz.*, those above 31°C, those below 31°C; and the one at 31°C.

(*a*) **Isotherms above 31°C.** The isotherm at 25°C is a rectangular hyperbola and approximates to the isotherm of ideal gas. So are all other isotherms above 31°C. Thus in the region

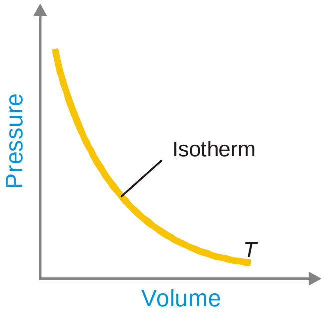

Figure 10.29
Isotherm of an ideal gas at temperature *T*.

above the isotherm at 31°C, carbon dioxide always exists in the gaseous state.

(*b*) **Isotherms below 31°C.** The isotherms below 31°C are discontinuous. For example, the isotherm of 21° consists of three parts.

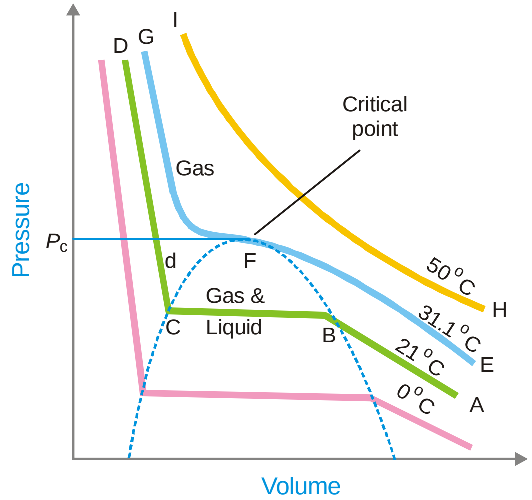

Figure 10.30

Andrews isotherms of CO_2 at different temperatures.

(*i*) *The curve AB*. It is a *PV* curve for gaseous carbon dioxide. Along *AB*, the volume decreases gradually with the increase of pressure. At *B* the volume decreases suddenly due to the formation of liquid carbon dioxide having higher density.

(*ii*) *The horizontal portion BC*. Along the horizontal part *BC* of the isotherm, the liquefaction continues while the pressure is held constant. At *C* all the gas is converted to liquid.

(*iii*) *The vertical curve CD*. This part of the isotherm is, in fact, the *P-V* curve of liquid carbon dioxide. This is almost vertical since the liquid is not very compressible.

(*c*) Isotherm at 31°C. Andrews noted that above 31°C there was no possibility of liquefaction of carbon dioxide however great the pressure applied. The **critical temperature** of carbon dioxide is, therefore, 31°C. The isotherm *EFG* at this temperature is called the **critical isotherm.** The *EF* portion of the critical isotherm represents the *P-V* curve of carbon dioxide gas. At the point *F*, the curve records a twist which is coincident with the appearance of liquid carbon dioxide. Here the gas and the liquid have the same density and are indistinguishable. The point is called the **critical point** and the corresponding pressure is called the **critical pressure** (72.7 atom). Beyond *F* the isotherm becomes nearly parallel to the vertical axis and marks the boundary between the gaseous carbon dioxide on the right and the liquid carbon dioxide on the left.

van der Waals' Equation and Critical Constants

Thomson (1871) studied the isotherms of carbon dioxide drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete **continuity of state** from gas to liquid. This he showed a theoretical wavy curve. The curve *MLB* in Fig. 10.31 represents a gas compressed in a way that it would remain stable. The curve *MNC* represents a superheated liquid. This type of continuity of state is predicated by van der Waals cubic equation. According to it, for any given values of *P* and *T* there should be three values of *V*. These values are indicated by points *B*, *M* and *C* of the wavy curve. The three values of *V* become closer as the horizontal part of the isotherm rises. At the critical point, these

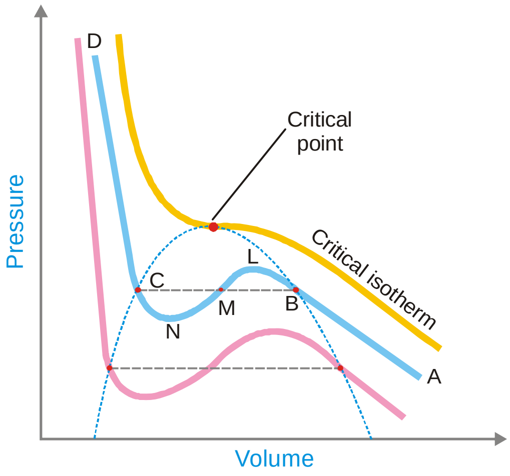

Figure 10.31

Isotherms of carbon dioxide according to van der Waals equation.

values become identical. *This enables the calculation of* T_c, P_c and V_c *in terms of van der Waals constants.* The van der Waals equation may be written as

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

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying the whole equation by V^2

or $$PV^3 - (RT + Pb)\,V^2 + aV - ab = 0$$

At the critical point

$$V^3 = V_c$$

$$(V - V_c)^3 = 0$$

or $$V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0 \qquad ...(1)$$

Thus at the critical point van der Waals equation gives

$$V^3 - \left(\frac{RT_c}{P_c} + b\right)V^2 + \left(\frac{a}{P_c}\right)V - \left(\frac{ab}{P_c}\right) = 0 \qquad ...(2)$$

Equating coefficients in (1) and (2)

$$3V_c = \frac{RT_c}{P_c} + b \qquad ...(3)$$

$$3V_c^2 = \frac{a}{P_c} \qquad ...(4)$$

$$V_c^3 = \frac{ab}{P_c} \qquad ...(5)$$

From (4) and (5)

$$V_c = 3b \qquad ...(6)$$

Substituting the value in (4)

$$P_c = \frac{a}{27b^2} \qquad \text{...(7)}$$

Substituting the values of V_c and P_c in (3)

$$T_c = \frac{8a}{27Rb} \qquad \text{...(8)}$$

Knowing *a* and *b* which can be deduced from deviations of ideal gas equation, the critical constants can easily be calculated. Conversely, since P_c and T_c can often be determined experimentally with comparative ease, these values may be employed to calculate the constants *a* and *b*.

$$a = 3\,V_c^2 P_c \qquad b = \frac{V_c}{3}$$

SOLVED PROBLEM 1. van der Waals' constants for hydrogen chloride gas are $a = 3.67$ atm lit^{-2} and $b = 40.8$ ml mol^{-1}. Find the critical temperature and critical pressure of the gas.

SOLUTION

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

$$= \frac{8 \times 3.67}{27 \times 0.0821 \times 0.0408} = 324.7\,\text{K}$$

$$= 51.7°\text{C}$$

$$P_c = \frac{a}{27b^2} = \frac{3.67}{27 \times (0.0408)^2}$$

$$= \mathbf{81.6\ atm}$$

SOLVED PROBLEM 2. The critical constants for water are $T_c = 647$ K, $P_c = 218$ atm, $V_c = 0.057$ litre/mol. Calculate van der Waals constants.

SOLUTION

$$a = 3\,P_c\,V_c^{\,2} = 3 \times 218 \times (0.057)^2$$

$$= 2.12\ \text{litre}^2\ \text{atm mol}^{-2}$$

$$b = \frac{V_c}{3} = \frac{0.057}{3}$$

$$= \mathbf{0.019\ litre\ mol^{-1}}$$

Experimental Determination of Critical Constants

The actual determination of critical constants of a substance is often a task of considerable difficulty. Of these the critical temperature and critical pressure can be measured relatively easily with the help of Cagniard de la Tour's apparatus. It consists of a stout glass U-tube blown into a bulb at the lower end. The liquid under examination is contained in the bulb and the rest of the apparatus is filled with mercury. The upper end of the U-tube is sealed leaving a little air in it so that this can be used as a manometer.

The temperature of the bulb containing the liquid and its vapour is raised gradually by means of the heating jacket. A point is reached when the meniscus of the liquid becomes faint and then disappears leaving the contents of the bulb perfectly homogeneous. On allowing the bulb to cool again, a mist first forms in the gas which quickly settles with the reappearance of the meniscus. **The mean of the temperatures of disappearance and reappearance of the meniscus in the bulb, is the**

critical temperature. The pressure read on the manometer at the critical temperature, gives the critical pressure.

The critical volume is the volume at critical temperature and critical pressure. It is much more difficult to measure since even a slight change in temperature of pressure at the critical point produces a large change in volume.

The most accurate method of determining the critical volume was given by Amagat. It consists of measuring the densities of a liquid and its vapour at a number of temperatures near the critical point, and plotting these two densities against the temperature. When the two curves representing the densities of the liquid and vapour thus drawn are extended, they naturally meet at the critical temperature because here the density of the liquid and vapour becomes identical.

The mean values of the densities are then plotted against the various temperatures where straight line *DC* is obtained which will obviously pass through the critical temperature which will be given by the point where this line will cut the curve *AB* (point *C* in Fig. 10.33). The density corresponding to the point *C* in the diagram is the **critical density.**

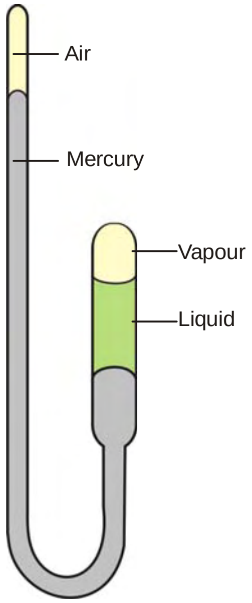

Figure 10.32
Cagniard de la Tour's apparatus.

The **critical volume** is obtained by dividing the molecular weight of the liquid by **critical density.**

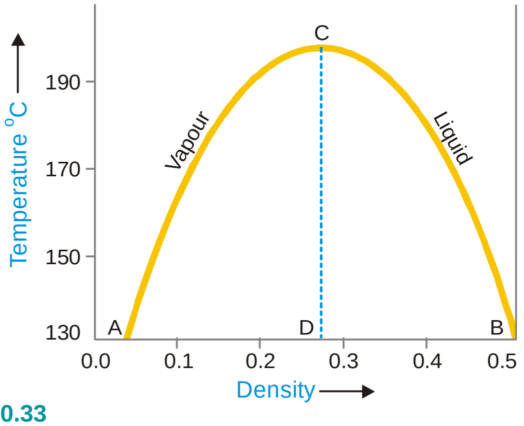

Figure 10.33
Illustration of the determination of critical volume (drawn for *n*-pentane).

The following Table gives the critical temperature and critical pressure of a few substances.

Substance	Critical temp (°C)	Critical pressure (Atm.)
Helium	–269	2.3
Hydrogen	–249	11
Nitrogen	–146	35
Oxygen	–119	51
Carbon dioxide	+31	73
Ammonia	+131	113
Water	+374	217
Ether	+194	35

LAW OF CORRESPONDING STATES

If the values of pressure, volume and temperature be expressed as fractions of the corresponding critical values, we have

$$\frac{P}{P_c} = \pi, \quad \frac{V}{V_c} = \phi, \quad \frac{T}{T_c} = \theta$$

where π, ϕ and θ are termed the **reduced pressure,** the **reduced volume,** and the **reduced temperature** respectively.

If now we replace P, V and T by πP_c, ϕV_c and θT_c respectively in van der Waals equation

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

we have,

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Substituting the values of P_c, V_c and T_c in terms of a, b and R as given in equation (6), (7) and (8), we get

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right)(3\phi b - b) = R\theta \frac{8a}{27\,Rb}$$

Dividing this equation throughout by $\frac{a}{27b^2}$, we get

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \qquad \text{...(9)}$$

This is known as **van der Waals reduced equation of state.** In this equation the quantities a, b, P_c, T_c, V_c which are characteristics of a given gas have cancelled out, thus making it applicable to all substances in the liquid or gaseous state irrespective of their specific nature. From equation (9) it is clear that **when two substances have the same reduced temperature and pressure, they will have the same reduced volume.** This is known as the **Law of Corresponding States** and when two or more substances are at the same reduced temperature and pressure, they are said to be in the **Corresponding states.** In practice this means that the properties of liquids should be determined at the same reduced temperature because pressure has very slight effect on them. Since it has been found that boiling points of liquids are approximately 2/3rd of the critical temperature, it follows that liquids are at their boiling points (in degrees absolute) approximately in corresponding states. Therefore in studying the relation between the physical properties of liquids and the chemical constitution, the physical properties may be conveniently determined at the boiling points of liquids.

SOLVED PROBLEM 1. The reduced volume (ϕ) and reduced temperature (θ) of a gas are 10.2 and 0.7. What will be its pressure if its critical pressure (P_c) is 4.25 atm ?

SOLUTION. It is given that

Reduced volume, ϕ = 10.2; Reduced temperature, θ = 0.7

Critical pressure, P_c = 4.25 atm

Applying reduced equations of state

$$\frac{3}{2}\ [3\ \ - 1]\quad 8$$

Substituting the values we get

LAW OF CORRESPONDING STATES

If the values of pressure, volume and temperature be expressed as fractions of the corresponding critical values, we have

$$\frac{P}{P_c} = \pi, \quad \frac{V}{V_c} = \phi, \quad \frac{T}{T_c} = \theta$$

where π, ϕ and θ are termed the **reduced pressure,** the **reduced volume,** and the **reduced temperature** respectively.

If now we replace P, V and T by πP_c, ϕV_c and θT_c respectively in van der Waals equation

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

we have,

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Substituting the values of P_c, V_c and T_c in terms of a, b and R as given in equation (6), (7) and (8), we get

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right)(3\phi b - b) = R\theta \frac{8a}{27\,Rb}$$

Dividing this equation throughout by $\frac{a}{27b^2}$, we get

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \qquad \text{...(9)}$$

This is known as **van der Waals reduced equation of state.** In this equation the quantities a, b, P_c, T_c, V_c which are characteristics of a given gas have cancelled out, thus making it applicable to all substances in the liquid or gaseous state irrespective of their specific nature. From equation (9) it is clear that **when two substances have the same reduced temperature and pressure, they will have the same reduced volume.** This is known as the **Law of Corresponding States** and when two or more substances are at the same reduced temperature and pressure, they are said to be in the **Corresponding states.** In practice this means that the properties of liquids should be determined at the same reduced temperature because pressure has very slight effect on them. Since it has been found that boiling points of liquids are approximately 2/3rd of the critical temperature, it follows that liquids are at their boiling points (in degrees absolute) approximately in corresponding states. Therefore in studying the relation between the physical properties of liquids and the chemical constitution, the physical properties may be conveniently determined at the boiling points of liquids.

SOLVED PROBLEM 1. The reduced volume (ϕ) and reduced temperature (θ) of a gas are 10.2 and 0.7. What will be its pressure if its critical pressure (P_c) is 4.25 atm ?

SOLUTION. It is given that

Reduced volume, $\phi = 10.2$; Reduced temperature, $\theta = 0.7$

Critical pressure, $P_c = 4.25$ atm

Applying reduced equations of state

$$\left[\pi + \frac{3}{\phi^2}\right][3\phi - 1] = 8\theta$$

Substituting the values we get

$$\left[\pi + \frac{3}{(10.2)^2}\right][3 \times 10.2 - 1] = 8 \times 0.7$$

or $$\left[\pi + \frac{3}{104.04}\right][30.6 - 1] = 5.6$$

or $$(\pi + 0.0288)\,(29.6) = 5.6$$

or $$\pi = \frac{5.6}{29.6} - 0.0288$$

$$= 0.18918 - 0.0288$$

$$= \mathbf{0.160389}$$

We know $$\frac{P}{P_c} = \pi$$

or $$P = \pi \times P_c = 0.016038 \times 4.25$$

$$= \mathbf{0.06816\ atm}$$

SOLVED PROBLEM 2. The critical temperature of hydrogen gas is 33.2°C and its critical pressure is 12.4 atm. Find out the values of ‘*a*’ and ‘*b*’ for the gas

SOLUTION. We know

$$T_c = \frac{8a}{27Rb} \quad ...(i); \qquad P_c = \frac{a}{27b^2} \quad ...(ii)$$

Dividing (*i*) by (*ii*) we get

$$\frac{T_c}{P_c} = \frac{8a}{27\,Rb} \times \frac{27\,b^2}{a} = \frac{8b}{R} \quad ...(iii)$$

Given $T_c = 33.2°\text{C} = 33.2 + 273 = 306.2\ \text{K}$

and $P_c = 12.4$ atm ; $R = 0.082$ atm. litre $\text{K}^{-1}\ \text{mol}^{-1}$

Substituting the values in equation (*iii*), we get

$$\frac{306.2}{12.4} = \frac{8 \times b}{0.082}$$

or $$b = \frac{306.2 \times 0.082}{12.4 \times 8}$$

$$= \mathbf{0.253\ litre\ mol^{-1}}$$

Now, substituting the value of ‘*b*’ in equation (*i*) we have

$$T_c = \frac{8a}{27Rb} \quad \text{or} \quad 306.2 = \frac{8 \times a}{27 \times 0.082 \times 0.253}$$

or $$a = \mathbf{21.439\ atm\ litre^2\ mol^{-1}}$$

METHODS OF LIQUEFACTION OF GASES

The general behaviour of gases with the decrease of temperature and increase of pressure is shown by the Andrews isotherms of CO_2 (Fig. 10.32). **If a gas is cooled below its critical temperature and then subjected to adequate pressure, it liquefies.** The various methods employed for the liquefaction of gases depend on the technique used to attain low temperature. The three important methods are :

(1) *Faraday's method* in which cooling is done with a freezing mixture

(2) *Linde's method* in which a compressed gas is released at a narrow jet (*Joule-Thomson effect*)

(3) *Claude's method* in which a gas is allowed to do mechanical work

FARADAY'S METHOD

Faraday (1823) used freezing mixtures of ice with various salts for external cooling of gases. The melting of ice and dissolution of salts both are endothermic processes. The temperature of the mixture is lowered up to a temperature when the solution becomes saturated.

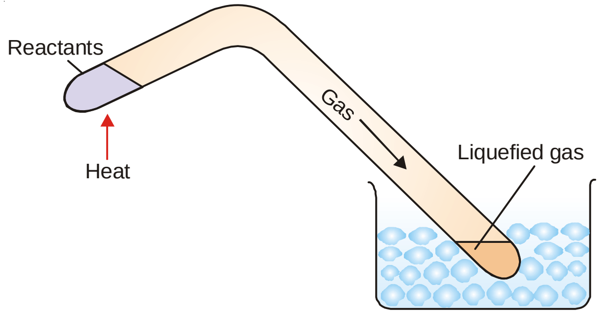

Figure 10.34

Faraday's method for the liquefaction of gases.

Faraday succeeded in liquefying a number of gases such as SO_2, CO_2, NO and Cl_2 by this method. He employed a V-shaped tube in one arm of which the gas was prepared. In the other arm, the gas was liquefied under its own pressure.

The gases liquefied by this method had their critical temperature above or just below the ordinary atmospheric temperature. The other gases including H_2, N_2 and O_2 having low critical points could not be liquefied by Faraday's method.

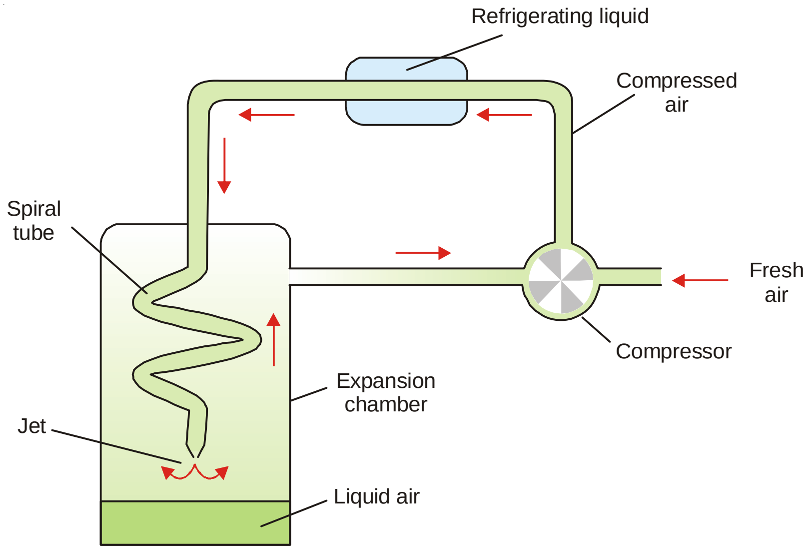

Figure 10.35

Linde's method for liquefaction of air.

LINDE'S METHOD

Linde (1895) used Joule Thomson effect as the basis for the liquefaction of gases. **When a compressed gas is allowed to expand into vacuum or a region of low pressure, it produces intense cooling.** In a compressed gas the molecules are very close and the attractions between them are appreciable. As the gas expands, the molecules move apart. In doing so, the intermolecular attraction must be overcome. The energy for it is taken from the gas itself which is thereby cooled.

Linde used an apparatus worked on the above principle for the liquefaction of air (see Fig. 10.35). Pure dry air is compressed to about 200 atmospheres. It is passed through a pipe cooled by a refrigerating liquid such as ammonia. Here, the heat of compression is removed. The compressed air is then passed into a spiral pipe with a jet at the lower end. The free expansion of air at the jet results in a considerable drop of temperature. The cooled air which is now at about one atmosphere pressure passed up the expansion chamber. It further cools the incoming air of the spiral tube and returns to the compressor. By repeating the process of compression and expansion, a temperature low enough to liquefy air is reached. The liquefied air collects at the bottom of the expansion chamber.

CLAUDE'S METHOD

This method for liquefaction of gases is more efficient than that of Linde. Here also the cooling is produced by free expansion of compressed gas. But in addition, the gas is made to do work by driving an engine. The energy for it comes from the gas itself which cools. **Thus in Claude's method the gas is cooled not only by overcoming the intermolecular forces but also by performance of work.** That is why the cooling produced is greater than in Linde's method.

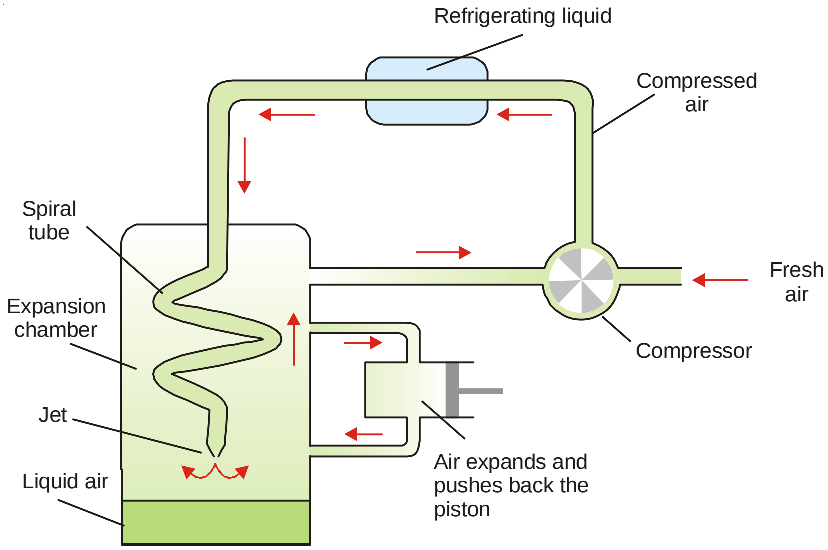

Figure 10.36

Claude's method for liquefaction of air.

Claude used the apparatus shown in Fig. 10.36. for the liquefaction of air. Pure dry air is compressed to about 200 atmospheres. It is led through a tube cooled by refrigerating liquid to remove any heat produced during the compression. The tube carrying the compressed air then enters the 'expansion chamber'. The tube bifurcates and a part of the air passes through the side-tube into the cylinder of an engine. Here it expands and pushes back the piston. Thus the air does mechanical work whereby it cools. The air then enters the expansion chamber and cools the incoming compressed air through the spiral tube. The air undergoes further cooling by expansion at the jet and liquefies. The gas escaping liquefaction goes back to the compressor and the whole process is repeated over and over again.

EXAMINATION QUESTIONS

1. Define or explain the following terms :

(*a*) Boyle's law
(*b*) Charle's law
(*c*) Absolute zero
(*d*) Avogadro's law
(*e*) Combined gas laws
(*f*) Ideal gas equation
(*g*) Gas constant
(*h*) Dalton's law
(*i*) Graham's law
(*j*) Mean free path
(*k*) Collision frequency
(*l*) Specific heat
(*m*) Molar heat capacity
(*n*) Real gases
(*o*) van der Waals equation
(*p*) Critical temperature
(*q*) Critical pressure
(*r*) Critical volume

2. At what temperature would ethane molecules have the same r.m.s. velocity as methane molecules at 27°C.

Answer. 289.5°C

3. (*a*) What is the law of corresponding states? How it is derived from the van der Waal's equation?

(*b*) Calculate the root mean square velocity of oxygen molecules at 27°C.

Answer. (*b*) 4.835×10^4 cm sec^{-1}

4. Calculate the critical constants (V_c, P_c and T_c) for C_2H_2 using van der Waal's constants $a = 4.390$ atm litre^2 moles^{-2}; $b = 0.05136$ litre mol^{-1} ($R = 0.082$ atm litre mol^{-1} K^{-1})

Answer. $V_c = 0.1540$ litre; $P_c = 61.63$ atm; $T_c = 15.86$ K

5. (*a*) Derive an expression for the pressure of an ideal gas by means of the kinetic theory and show that the total kinetic energy of the molecules in one mole of an ideal gas is equal to $3/2RT$.

(*b*) Calculate the root mean square velocity of oxygen molecules at 25°C.

Answer. 4.819×10^4 cm sec^{-1}

6. (*a*) Derive the kinetic gas equation for an ideal gas.

(*b*) Calculate the root mean square velocity for oxygen molecules at 26.85°C, given that gas constant is 8.314×10^7 ergs mol^{-1} deg^{-1}.

Answer. 4.8365×10^4 cm sec^{-1}

7. (*a*) What are assumptions of kinetic theory of gases and show how far are they justified?

(*b*) A vessel of volume 1.0 litre contains 10^{25} gas molecules of mass 10^{-24} g each. If the r.m.s. velocity is 10^5 cm sec^{-1}, calculate the total kinetic energy and the temperature.

Answer. (*b*) 5×10^{10} ergs; 127.93°C

8. (*a*) Derive van der Waal's reduced equation of state. Explain the significance of the law.

(*b*) Critical density of a substance having molecular weight is 0.555 gm/cc and $P_c = 48$ atm. Calculate van der Waal's constants '*a*' and '*b*'.

Answer. (*b*)$a = 5.645$ atm litre^2 mol^{-2}; $b = 0.066$ litre mol^{-1}

9. (*a*) Indicate what do you mean by 'mean' and r.m.s. velocity of gas molecules.

(*b*) Calculate the root mean square (rms) speed of CO_2 molecules at 27°C.

(*c*) Define critical constants of a gas. Obtain the relation from van der Waal's gas.

$$\frac{RT_c}{P_cV_c} = \frac{8}{3}$$

where symbols have their usual meanings.

Answer. (*b*) 4.1238×10^4 cm sec^{-1}

10. For ammonia gas van der Waals constants *a* and *b* are 4.0 litre^2 atm mol^{-2} and 0.036 litre mol^{-1} respectively. Calculate critical volume. ($R = 0.082$ litre atm deg^{-1})

Answer. 0.108 lit.

11. (*a*) What do you understand by the distribution of molecular velocities of a gas? Illustrate your answer with the help of a diagram.

(*b*) Calculate the root mean square velocity of CO_2 at 27°C.

Answer. 4.124×10^4 cm sec^{-1}

12. (*a*) Discuss the causes of deviation of real gases from ideal gas behaviour. How are they accounted for in the van der Waal's equation?

(*b*) What is the 'mean free path' of a gas? Give its relationship with the collision diameter as well as with the viscosity of a gas. (*Delhi BSc, 2000*)

13. Write short note on 'critical constants and their experimental determination'. (*Lucknow BSc, 2001*)

14. (*a*) Prove that for gases $C_p - C_v = R$. Define the terms involved. How does it help in determining the aromaticity of the gases?

(*b*) Explain the law of corresponding state. (*Lucknow BSc, 2001*)

15. (*a*) How and why real gases deviate from ideal behaviour. Derive van der Waal's equation for '*n*' moles.

(*b*) What do you understand by the mean free path and collision diameter of a gas molecule. Give the effect of temperature and pressure on the free path. (*Lucknow BSc, 2001*)

16. Calculate critical constants V_c, P_c and T_c for C_2H_2 using van der Waal's constants.

$a = 4.39$ atm lit mol^{-1}, $b = 0.5316$ litre mol^{-1}. ($R = 0.082$ litre atm K^{-1} mol^{-1})

Answer. 1.5948 litre; 0.575 atm and 29.83 K (*Delhi BSc, 2001; Nagpur BSc, 2002*)

17. (*a*) What are the limitations of the equation $PV = RT$? What improvements have been suggested by van der Waal?

(*b*) How van der Waal's equation can be applied for the calculation of Boyle's temperature? Also define Boyle's temperature.

(*c*) Show that van der Waal's equation reduces to ideal gas equation at Boyle's temperature.

(*MD Rohtak BSc, 2002*)

18. Define critical constants. Explain the experimental determination of critical constants.

(*Sri Venkateswara BSc, 2002*)

19. (*a*) How does the van der Waal's equation explain the behaviour of gases at

(*i*) High pressure and (*ii*) Low pressure

(*b*) Discuss the critical constants of a gas. (*Jamia Millia BSc, 2002*)

20. Calculate the average internal energy of a diatomic molecule at 300 K using law of equipartition of energy.

Answer. 6235.5 J (*Panjab BSc, 2002*)

21. Calculate average velocity of oxygen molecule at 25°C. ($R = 8.314$ JK^{-1} mol^{-1})

Answer. 444.138 m sec^{-1} (*Nagpur BSc, 2002*)

22. Explain the deviation of real gases from ideal gas behaviour and derive the van der Waal's equation for one mole of a gas

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

(*Allahabad BSc, 2002*)

23. (*a*) What is Boyle's temperature? Give its significance.

(*b*) Define specific heat and heat capacity. What is the difference between the two?

(*c*) Describe the temperature dependence of molecular distribution of energies.

(*Guru Nanak Dev BSc, 2002*)

24. (*a*) Explain the term degree of freedom.

(*b*) State law of corresponding state. (*Nagpur BSc, 2002*)

25. Derive the van der Waal's equation for *n* moles of a gas and write down the units in which van der Waal's constants are expressed. (*Arunachal BSc, 2002*)

26. Calculate the root mean square velocity of nitrogen molecule at 27°C.

Answer. 1.63×10^5 cm sec^{-1} (*Vidyasagar BSc, 2002*)

27. (*a*) If the equation of state for one mole of a gas is $P(v - b) = RT$, find the value of

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V$$

(*b*) Show that $C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$ and hence for an ideal gas (1 mole) $C_p - C_v = R$

(*c*) Show that at equilibrium : $(\partial G)_{T,\,P} = 0,\ (\partial A)_{T,\,V} = 0$ (*Jamia Millia BSc, 2002*)

28. (*a*) What are ideal and non-ideal gases? Explain why the real gases deviate from ideal behaviour?

(*b*) The critical volume of a gas is 0.105 L mol^{-1}. Assuming the molecules of the gas to be spherical, calculate the diameter of the gas molecule.

Answer. (*b*) 4.806×10^{-9} m (*Guru Nanak Dev BSc, 2002*)

29. (*a*) What is kinetic gas equation? Derive Boyle's law and Charle's law from it.

(*b*) Define mean free path and collision diameter.

(*c*) On the basis of kinetic theory of gases, show that for monoatomic gases $C_p - C_v = R$.

(*Punjabi BSc, 2002*)

30. (*a*) Explain the significance of van der Waal's constant.

(*b*) Why do gases fail to obey ideal gas equation at high pressure and low temperature?

(*Punjabi BSc, 2002*)

31. (*a*) What are the real gases? In which conditions real gases deviate from ideal gas behaviour? Describe these deviations and derive van der Waal's equation.

(*b*) What do you understand by the liquefaction of gases. Describe two methods briefly.

(*HS Gaur BSc, 2002*)

32. (*a*) Deduce Avogadro's law from the kinetic gas equation.

(*b*) What will be the real gas equation if the pressure is too high?

(*c*) Why is volume correction necessary for a real gas? What is the unit of '*b*'.

(*Arunachal BSc, 2002*)

33. State the principle of equipartition of energy and explain the high temperature limiting value of molar heat capacity of a diatomic molecule at constant volume can be evaluated with the help of this principle.

(*Vidyasagar BSc, 2002*)

34. What is compressibility factor? How van der Waal's equation of state accounts for the non-ideal behaviour of gases? (*Aligarh BSc, 2002*)

35. (*a*) What do you understand by C_p and C_v of gases?

(*b*) State Kirchoff's law. (*Madurai BSc, 2002*)

36. Write down the expression for the Maxwell's distribution of molecular speed and discuss its characteristics. (*Vidyasagar BSc, 2002*)

37. (*a*) Explain how real gases deviate from ideal behaviour. What are the causes of deviations.

(*b*) What is the law of corresponding states? Deduce the equation for law of corresponding states.

(*Arunachal BSc, 2002*)

38. (*a*) What is meant by degree of freedom of a molecule? How is it classified into different forms.

(*b*) Explain giving reasons why the heat capacity of a diatomic gas is greater than that of a monoatomic gas. Show that the ratio C_p / C_v for monoatomic gases is 1.66. (*Mizoram BSc, 2002*)

39. (*a*) Write the wrong assumptions of kinetic theory of gases and derive the van der Waal's equation.

(*b*) Explain deviation of gases from ideal gas behaviour with the help of a graph.

(*Jamia Millia BSc, 2002*)

40. (*a*) What are the van der Waal's forces? How do they originate in non-polar molecules? Explain giving examples.

(*b*) Calculate molecular diameter of helium. Given $b = 2.4 \times 10^{-3}$ m^{-1} mol^{-1}

Answer. (*b*) 4.238×10^{-10} m

41. Derive the reduced equation of state for a gas obeying van der Waal's equation (Assume the necessary expression for P_c, V_c, and T_c. Explain significance. (*Vidyasagar BSc, 2002*)

42. Derive the relation between C_p and C_v for an ideal gas. (*Nagpur BSc, 2002*)

43. (*a*) Write the expression for the distribution of molecular velocities. What is root mean square velocity?

(*b*) Explain the principle of continuity of state. (*Aligarh BSc, 2002*)

44. Starting from kinetic gas equation derive

(*i*) Avogadro's law; and (*ii*) Graham's law of diffusion (*Nagpur BSc, 2003*)

45. Calculate the root mean square velocity of hydrogen gas at 0°C. ($R = 8.314$ JK^{-1} mol^{-1})

Answer. 184.51×10^3 cm sec^{-1} (*Arunachal BSc (H), 2003*)

46. What are ideal and non-ideal gases? What are the chief causes of deviation of real gases from ideal behaviour? Derive van der Waal's equation and show how these are accounted for in this equation.

(*Guru Nanak Dev BSc, 2003*)

47. Show that the total pressure (*P*) exerted by an ideal gas containing '*N*' molecules and occupying volume '*V*' is given by :

$$P = \frac{m\,N\,\mu^2}{3\,V}$$

(*Guru Nanak Dev BSc, 2002*)

48. What is critical phenomenon? Derive expression for the critical constants of a gas using van der Waal's equation of state. How do you find out the van der Waal's constants from the critical values of pressure, temperature and volume? (*Sambalpur BSc, 2003*)

49. (*a*) Explain why beyond a certain temperature gases can not be liquefied whatever the pressure may be.

(*b*) Describe the effect of temperature and pressure on mean free path.

(*c*) Describe law of corresponding state. (*Guru Nanak Dev BSc, 2003*)

50. (*a*) Expected values of heat capacities for gases are observed only at high temperatures. Explain.

(*b*) The compressibility factor is unity at Boyle temperature of gas. Why?

(*c*) Calculate '*r*' for diatomic molecule using equipartition principle. (*Sambalpur BSc, 2003*)

51. (*a*) Discuss the effect of temperature on molecular velocity.

(*b*) Derive a relationship between C_p and C_v for an ideal gas. (*Nagpur BSc, 2003*)

52. At what temperature would ethane molecule have the same r.m.s. velocity as methane molecules at 27°C?

Answer. 562.4 K (*Delhi BSc, 2003*)

53. (*a*) Derive the reduced equation of state for a gas.

(*b*) What is the law of corresponding states? (*Delhi BSc, 2003*)

54. Find the relationship between kinetic energy and temperature. (*Arunachal BSc, 2003*)

55. A 10.0 L flask contains 64 g of oxygen at 27°C. Calculate its pressure using

(*i*) van der Waal's equation and (*ii*) ideal gas equation

Given that $a = 4.17$ atm L mol^{-2} and $b = 0.037$ L mol^{-1}

Answer. 4.808 atm; 4.938 atm (*Arunachal BSc (H), 2003*)

56. (*a*) What is kinetic gas equation? Explain the concept of absolute zero.

(*b*) What do you understand by the degree of freedom of motion. Briefly explain the different type of degrees of freedom possessed by linear and non-linear molecules. (*Panjab BSc, 2002*)

57. (*a*) Deduce the equation for mean free path of a gas molecule and hence show that how it varies with temperature and pressure.

(*b*) Explain using different curves that real gases can behave ideally at very low pressure and at fairly high temperature. (*Kalyani BSc, 2003*)

58. Starting from van der Waal's equation, derive the values of critical volume and critical pressure in terms of van der Waal's constants '*a*' and '*b*'. van der Waal's constants for carbon dioxide are $a = 3.6$ atm dm^6 mol^{-2} and $b = 4.28 \times 10^{-2}$ dm^3 mol^{-1}. Calculate critical volume and critical pressure of the gas.

Answer. $V_c = 1.284 \times 10^{-1}$ atm dm^6 mol^{-2}; $P_c = 1.03$ atm dm^3 mol^{-1} (*Nagpur BSc, 2003*)

59. Calculate RMS velocity of methane molecule at 370 K ($R = 8.314$ JK^{-1} mol^{-1}, $M = 16 \times 10^{-3}$ kg)

Answer. 7.5946×10^4 cm sec^{-1} (*Nagpur BSc, 2003*)

60. Oxygen has a density of 1.429 g per litre at NTP. Calculate the r.m.s. and average velocity of its molecules.

Answer. 1.3487×10^3 cm sec^{-1}; 1.2426×10^3 cm sec^{-1} (*Delhi BSc, 2003*)

61. (*a*) What is meant by root mean square velocity of gaseous molecules? How is it different from average velocity?

(*b*) Calculate the average kinetic energy per molecule of CO_2 gas at 27°C. ($R = 1.987$ cal deg^{-1} mol^{-1})

Answer. (*b*) 894.15 cal (*Sambalpur BSc, 2003*)

62. What do you mean by fugacity? Explain clearly that the fugacity of a gas can be less than as well as more than the pressure. (*Arunachal BSc, 2003*)

63. Oxygen has a density of 1.429 g litre at NTP. Calculate the r.m.s. and average velocity of its molecules.

Answer. 0.4612 m sec^{-1}; 0.4249 m sec^{-1} (*Delhi BSc, 2003*)

64. (*a*) What were the reasons which led van der Waals to modify the ideal gas equation. Write down the modified equation.

(*b*) One mole of diethyl ether occupies 15 litres at 227°C. Calculate the pressure if van der Waal's constants for diethyl ether are $a = 17.38$ atm $litre^2$ mol^{-2} and $b = 0.134$ litre mol^{-1}.

Answer. 2.6184 atm (*Anna BSc, 2004*)

65. (*a*) Write van der Waal's equation. What are the limitations of this equation? Give the units of van der Waal's constants.

(*b*) Define mean free path and collision frequency. Explain how mean free path depends upon collision frequency and molecular size.

(*c*) Calculate the critical temperature of a van der Waal's gas for which P_c is 100 atm. and *b* is 50 cm^3 mol^{-1}.

Answer. (*c*) 214.2°C (*Mangalore BSc, 2004*)

66. (*a*) Distinguish between root mean square velocity and most probable velocity.

(*b*) Calculate molar volume of an ideal gas at 127°C and 1 atm. pressure.

(*c*) Why van der Waal's equation is applicable to real gases? Define compressibility factor and Boyle's temperature.

Answer. (*b*) 32.84 litre (*Burdwan BSc, 2004*)

67. Two gases P and Q having molecular masses 44 and 64 respectively are enclosed in a vessel. Their masses are 0.5 g and 0.3 g respectively and the total pressure of the mixture is 740 mm. Calculate the partial pressures of the two gases.

Answer. 524 mm ; 216 mm (*Burdwan BSc, 2005*)

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

Answer. 0.492 atm ; 0.246 atm (*Arunachal BSc, 2005*)

69. Calculate the average kinetic energy in Joules of the molecules in 8.0 g of methane at 27 ºC.

Answer. 1870.65 J (*Mysore BSc, 2005*)

70. Calculate the root mean square velocity of Ozone kept in a closed vessel at 20 ºC and 82 cm mercury pressure.

Answer. 3.9032×10^4 cm sec^{-1} (*Purvanchal BSc, 2005*)

71. Calculate the volume occupied by 7 g of nitrogen gas at 27 ºC and 750 mm pressure.

Answer. 6.23 litre (*Kalyani BSc, 2006*)

73. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 27 ºC and 27 atm pressure. If the cylinder can hold 2.82 litre of water, calculate the number of balloons that can be filled up.

Answer. 10 (*Jamia Millia BSc, 2006*)

74. Calculate the total pressure in a mixture of 4 g of oxygen and 3 g of hydrogen confined in a total volume of one litre at 0 ºC.

Answer. 25.18 atm (*Mumbai BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. According to Boyle's law the volume of a fixed mass of a gas, at constant temperature, is

(*a*) directly proportional to its pressure
(*b*) inversely proportional to its pressure
(*c*) the square root of its pressure
(*d*) none of these

Answer. (*b*)

2. Mathematically, Boyle's law can be represented as

(*a*) $V \propto 1/P$
(*b*) $V = k/P$
(*c*) $V P = k$
(*d*) all of these

Answer. (*d*)

3. At constant temperature, the pressure of the gas is reduced to one third, the volume

(*a*) reduces to one third
(*b*) increases by three times
(*c*) remains the same
(*d*) cannot be predicted

Answer. (*b*)

4. At constant pressure, the volume of a fixed mass of a gas is

(*a*) directly proportional to its temperature
(*b*) directly proportional to its absolute temperature
(*c*) inversely proportional to its temperature
(*d*) inversely proportional to its absolute temperature

Answer. (*b*)

5. Which of the following is the correct mathematical relation for Charle's law at constant pressure?

(*a*) $V \propto T$
(*b*) $V \propto t$
(*c*) $V = kt$
(*d*) none of these

Answer. (*a*)

6. According to Gay Lussac's law for a fixed volume of a given gas

(*a*) P/T = a constant
(*b*) $P \propto 1/T$
(*c*) $P = k/T$
(*d*) $PT = k$

Answer. (*a*)

7. "Equal volume of all gases at the same temperature and pressure contain equal number of molecules" is the statement of

(*a*) combined gas law (*b*) Charle's law

(*c*) Avogadro's law (*d*) Boyle's law

Answer. (*c*)

8. For one mole of a gas, the ideal gas equation is

(*a*) $PV = RT$ (*b*) $PV = 1/2\ RT$

(*c*) $PV = 3/2\ RT$ (*d*) $PV = 5/2\ RT$

Answer. (*a*)

9. The units of *R*, the gas constant are

(*a*) erg K^{-1} mol^{-1} (*b*) cal K^{-1} mol^{-1}

(*c*) joule K^{-1} mol^{-1} (*d*) all of these

Answer. (*d*)

10. In lit atm K^{-1} mol^{-1} the numerical value of *R*, the gas constant, is

(*a*) 0.821 (*b*) 0.0821

(*c*) 0.00821 (*d*) 0.000821

Answer. (*b*)

11. "The total pressure of a mixture of gases (non–reacting) is equal to the sum of the partial pressures of all the gases present" is the statement of

(*a*) Graham's law of diffusion (*b*) Dalton's law of partial pressures

(*c*) Avogadro's law of partial pressures (*d*) none of these

Answer. (*b*)

12. Under same conditions of temperature and pressure, the rates of diffusion of different gases are

(*a*) directly proportional to the square roots of the molecular masses

(*b*) directly proportional to the square roots of their vapour densities

(*c*) inversely proportional to the square roots of their molecular masses

(*d*) inversely proportional to the square roots of their molar volumes

Answer. (*c*)

13. The average kinetic energy of the gas molecules is

(*a*) inversely proportional to its absolute temperature

(*b*) directly proportional to its absolute temperature

(*c*) equal to the square of its absolute temperature

(*d*) directly proportional to the square root of its absolute temperature

Answer. (*b*)

14. For one mole of a gas the kinetic energy is given by

(*a*) $E = 1/2\ RT$ (*b*) $E = 3/2\ RT$

(*c*) $E = 5/2\ RT$ (*d*) $E = 7/2\ RT$

Answer. (*b*)

15. The kinetic gas equation is given by the relation

(*a*) $PV = 1/3\ m\ N\ \mu^2$ (*b*) $PV = 1/2\ m\ N\ \mu^2$

(*c*) $PV = 3/2\ m\ N\ \mu^2$ (*d*) $PV = 2/3\ m\ N\ \mu^2$

Answer. (*a*)

16. The average velocity of a gas is given by

(*a*) $\bar{v} = \sqrt{\dfrac{8RT}{n\ M}}$ (*b*) $\bar{v} = \sqrt{\dfrac{3RT}{n\ M}}$

(*c*) $\bar{v} = \sqrt{\frac{2RT}{n\,M}}$ (*d*) $\bar{v} = \sqrt{\frac{RT}{n\,M}}$

Answer. (*a*)

17. The root mean square velocity of gas molecules is given by the relation

(*a*) $\mu = \sqrt{\frac{RT}{M}}$ (*b*) $\mu = \sqrt{\frac{2RT}{M}}$

(*c*) $\mu = \sqrt{\frac{3RT}{M}}$ (*d*) $\mu = \sqrt{\frac{8RT}{M}}$

Answer. (*c*)

18. The root mean square velocity gas molecules is given by the relation

(*a*) $\mu = \sqrt{\frac{3PV}{M}}$ (*b*) $\mu = \sqrt{\frac{3RT}{M}}$

(*c*) $\mu = \sqrt{\frac{3P}{D}}$ (*d*) all of these

Answer. (*d*)

19. The free path is the distance travelled by the molecule

(*a*) before collision (*b*) in one second

(*c*) after collision (*d*) in one minute

Answer. (*a*)

20. The mean free path is

(*a*) directly proportional to the pressure of the gas

(*b*) directly proportional to the root mean square velocity of gas

(*c*) directly proportional to the temperature of the gas

(*d*) directly proportional to the absolute temperature of the gas

Answer. (*d*)

21. The collision frequency of a gas is

(*a*) directly proportional to the square root of absolute temperature

(*b*) directly proportional to the absolute temperature

(*c*) inversely proportional to the pressure of the gas

(*d*) inversely proportional to the absolute temperature

Answer. (*b*)

22. The value of γ, the specific heat ratio, for a monoatomic gas is

(*a*) 0 (*b*) 1.40

(*c*) 1.667 (*d*) 1.33

Answer. (*a*)

23. The compressibility factor, *z* *i.e.* the extent to which a real gas deviates from ideal behaviour is given by

(*a*) $z = \frac{PV}{RT^2}$ (*b*) $z = \frac{PV}{2RT}$

(*c*) $z = \frac{PV}{RT}$ (*d*) $z = \frac{2PV}{RT}$

Answer. (*c*)

24. The real gases show nearly ideal behaviour at

(*a*) low pressures and low temperatures (*b*) high pressures and low temperatures

(*c*) high pressures and high temperatures (*d*) low pressures and high temperatures

Answer. (*d*)

25. Excluded volume is _____ times the actual volume of molecules.

(*a*) ½ (*b*) two

(*c*) three (*d*) four

Answer. (*d*)

26. The pressure P in the ideal gas equation is replaced by

(*a*) $\left(P + \frac{a\,n^2}{V^2}\right)$ (*b*) $\left(P - \frac{a\,n^2}{V^2}\right)$

(*c*) $\left(P + \frac{2\,n^2}{V^2}\right)$ (*d*) $\left(P + \frac{n^2}{2\,V^2}\right)$

Answer. (*a*)

27. The units of '*a*' the van der Waal's constant are

(*a*) atm lit mol^{-1} (*b*) atm lit^{-1} mol^{-1}

(*c*) atm lit^{-2} mol^{-2} (*d*) atm lit^{-1} mol^{-2}

Answer. (*c*)

28. Which one of the following is incorrect?

(*a*) the critical temperature, T_c, of a gas is that temperature above which it can be liquefied no matter how high pressure is applied

(*b*) the critical pressure, P_c , is the minimum pressure required to liquefy the gas at its critical temperature

(*c*) the critical volume, P_c , is the volume occupied by one mole of the gas at critical temperature and critical volume

(*d*) none of these

Answer. (*d*)

29. Which one of the following relations is correct?

(*a*) $V_c = 3b$ (*b*) $P_c = \frac{a}{27\,R\,b^2}$

(*c*) $T_c = \frac{8a}{27\,R\,b}$ (*d*) none of these

Answer. (*d*)

30. The van der Waal's reduced equation of state is

(*a*) $\left[\pi + \frac{3}{\phi^2}\right](3\,\phi - 1) = 8\theta$ (*b*) $\left[\pi - \frac{3}{\phi^2}\right](3\,\phi + 1) = 8\theta$

(*c*) $\left[\pi + \frac{3}{\phi}\right](3\,\phi + 1) = 8\theta$ (*d*) $\left[\pi + \frac{3}{\phi^2}\right]\left(\frac{\phi}{3} + 1\right) = 8\theta$

Answer. (*a*)

31. How many molecules are present in 0.2 g of hydrogen?

(*a*) 6.023×10^{23} (*b*) 6.023×10^{22}

(*c*) 3.0125×10^{23} (*d*) 3.0125×10^{22}

Answer. (*b*)

32. Gas A diffuses twice as fast as another gas B. If the vapour density of the gas A is 2, the molecular mass of gas B is

(*a*) 2 (*b*) 4

(*c*) 8 (*d*) 16

Answer. (*d*)

33. A container contains a gas at 1 atm pressure. To compress it to 1/3rd of its initial volume, pressure to be applied is

(*a*) 1 atm
(*b*) 2 atm
(*c*) 3 atm
(*d*) 6 atm

Answer. (*c*)

34. The ratio of most probable velocity, average velocity and root mean square velocity of molecules of a gas is

(*a*) 1 : 1.128 : 1.224
(*b*) 1.128 : 1 : 1.224
(*c*) 1.128 : 1.224 : 1
(*d*) 1.224 : 1 : 1.128

Answer. (*a*)

35. Which of the following gases will have the highest rate of diffusion?

(*a*) CH_4
(*b*) NH_3
(*c*) N_2
(*d*) CO_2

Answer. (*a*)

36. 290 ml of a gas at 17°C is cooled to –13°C at constant pressure. The new volume of the gas will be

(*a*) 260 ml
(*b*) 270 ml
(*c*) 280 ml
(*d*) 290 ml

Answer. (*a*)

37. The volume of a gas at 0°C is 273 ml. Its volume at 12°C and the same pressure will be

(*a*) $273 + \frac{12}{273}$ ml
(*b*) $273 + \frac{273}{12}$ ml
(*c*) 273 + 12 ml
(*d*) 273 – 12 ml

Answer. (*c*)

38. If the pressure and absolute temperature of 3 litres of a gas are doubled, its volume would be

(*a*) 2 litres
(*b*) 3 litres
(*c*) 6 litres
(*d*) 12 litres

Answer. (*b*)

39. The mass of 2240 ml of CO_2 at NTP will be

(*a*) 4.0 g
(*b*) 4.4 g
(*c*) 8.8 g
(*d*) 8.0 g

Answer. (*b*)

40. The mass of 224 ml of N_2 on liquefaction will be

(*a*) 28 g
(*b*) 14 g
(*c*) 1.4 g
(*d*) 2.8 g

Answer. (*d*)

41. The root mean square velocity of a certain gas at 27°C is y cm sec^{-1}. The temperature at which its velocity will be $2y$ is

(*a*) 54°C
(*b*) 108°C
(*c*) 600 K
(*d*) 1200 K

Answer. (*d*)

42. Out of the following pairs of gases, which will diffuse through a porous plug with the same rate of diffusion?

(*a*) NO, CO
(*b*) CH_4, O_2
(*c*) NO_2, CO_2
(*d*) NO, C_2H_6

Answer. (*d*)

43. 8 g of CH_4 and 2 g of hydrogen are mixed and kept at 760 mm pressure at 273 K. The total volume occupied by the mixture will be

(*a*) 11.2 litre
(*b*) 22.4 litre

(*c*) 33.6 litre (*d*) 44.8 litre

Answer. (*c*)

44. The root mean square velocity of a certain gas at 27°C is a m $\sec^{-1}$. Its root mean square velocity at 927°C is

(*a*) $a/2$ m $\sec^{-1}$ (*b*) $2a$ m $\sec^{-1}$

(*c*) $3a$ m $\sec^{-1}$ (*d*) $6a$ m $\sec^{-1}$

Answer. (*b*)

45. In a closed flask of one litre, 2.0 g of hydrogen gas is heated from 27°C to 327°C. Which of the following is incorrect?

(*a*) the pressure of the gas increases

(*b*) the kinetic energy of gaseous molecules increases

(*c*) the rate of collision increases

(*d*) the number of moles of the gas increases

Answer. (*d*)

46. Which of the following gases will have the lowest rate of diffusion?

(*a*) H_2 (*b*) N_2

(*c*) F_2 (*d*) O_2

Answer. (*c*)

47. A gas is heated at constant temperature. Then

(*a*) the no. of molecules of the gas increases

(*b*) the kinetic energy of the gas molecules decreases

(*c*) the kinetic energy of the gas molecules remains unaltered

(*d*) the kinetic energy of the gas molecules increases

Answer. (*c*)

48. Equal volumes of methane and ethane are mixed in an empty container at 25°C. The fraction of total pressure exerted by ethane is

(*a*) 1/2 (*b*) 2/3

(*c*) 8/15 (*d*) 3/2

Answer. (*a*)

49. In van der Waal's equation of state for a non-ideal gas the net force of attraction among the molecules is given by

(*a*) $\frac{a\,n^2}{V^2}$ (*b*) $P + \frac{a\,n^2}{V^2}$

(*c*) $P - \frac{a\,n^2}{V^2}$ (*d*) $-\frac{a\,n^2}{V^2}$

Answer. (*a*)

50. The compressibility factor, z, for an ideal gas is

(*a*) zero (*b*) less than one

(*c*) greater than one (*d*) equal to one

Answer. (*d*)

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