

11

PROPERTIES OF GASES

11.1 INTRODUCTION

As you have studied in the previous lessons, all the matters are found in three states — solid, liquid and gas. They are composed of molecules. The molecules have certain inter-molecular forces and thermal energy. When the mean thermal energy is increased, a stage comes when the molecules become completely free from each other i.e. the intermolecular force between them vanishes. However, they have enough chances to collide against each other. This state of matter is said to be gaseous state. In the gaseous state the matters (substances) don't have definite shape and size. The gases occupy the shape and size of the container in which they are filled.

Under different conditions of temperature, pressure and volume, gases exhibit different properties. For example when the temperature of gas is increased at constant volume, its pressure increases. Can you explain why? Though you may have feeling of such concepts. After studying this lesson you will find the exact explanation of such concepts. In this lesson you will study about the kinetic theory of gases which explain properties of gases. You will also study about the kinetic interpretation of temperature and the relationship between the kinetic energy of the molecules and the temperature. Why the gases have two types of specific heats will also be answered in this lesson.

11.2. OBJECTIVES

After studying this lesson, you should be able to:

- state the assumptions of kinetic theory of gases; and
 - derive the expression for pressure $P = \frac{1}{3} \rho C^2$
 - distinguish between the RMS velocity and the average velocity of molecules and establish their relationship with temperature;
 - derive gas laws such as (a) Boyle's law, (b) Charle's law, (c) Pressure-temperature law, (d) Avogadro's law, and (e) Dalton's law, of partial pressure, on the basis of kinetic theory of gases.
 - give kinetic interpretation of temperature and compute the mean kinetic energy of a gas;
 - explain law of equipartition of energy;
 - give reasons for the existance of two specific heats of gas, define them; and
 - derive the relation $C_p - C_v = R/J$.
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11.3 KINETIC THEORY OF GASES

We are already aware that matter is composed of very large number of atoms and molecules. Each of these molecules show the characteristic properties of the substance of which it is a part. John Dalton in 1803 made use of this concept of matter that is, matter is composed of large number of molecules. Later it was found that the molecules of substance are in constant motion. This led to the development of kinetic theory of matter.

Now let us see how a gas fills a container. In a gas the molecules are so far apart from each other that there is little intermolecular attraction. The cohesive force (which binds molecules together) between the particles of matter which constitutes a gas is thus extremely small. It is due to this reason that a gas fills a container completely in which it is kept.

The kinetic theory has been developed in the case of gases. The mathematical basis of the kinetic theory of gases was established by Maxwell and Clausius.

The kinetic theory of gases attempts to relate the macroscopic properties such as pressure, volume and temperature of an ideal gas with its microscopic properties such as speed and mass of its molecules. At this point the terms macroscopic and microscopic need a little elaboration. Macroscopic simply means, pertaining to a whole assembly of a large number of molecules. Microscopic on the other hand is confined to quantities concerning with individual molecule. According to the kinetic theory of gases, the molecules of velocities making collisions for a short time with each other and with the walls of the container and rebounding from them. This motion of molecules is random. The kinetic theory makes certain assumptions.

11.3.1 Assumption of Kinetic Theory of Gases

Clark Maxwell in 1860 showed that the well known properties of a gas can be explained on the basis of certain assumptions which are called as the assumptions of kinetic theory of gases.

- (i) a gas consists of a very large number of small molecules which are considered to be rigid, and identical in all respects and moving with all possible velocities in all possible directions the intermolecular forces are negligible.
- (ii) the collisions between the molecules and against the walls of container are perfectly elastic
- (iii) the volume of the molecules themselves is negligible as compared to the volume occupied by the gas.
- (iv) between collisions the molecules move in a straight line with uniform velocity.
- (v) the time taken in a collision is negligible as compared to the time interval by a molecule between two successive collisions.

vi) distribution of molecules is uniform throughout the container.

Let us first consider motion along the axis. *OX*. (Fig. 11.1). Since the mass of the molecules is m and it is moving with a speed u , therefore, its momentum will be mu towards the wall *X*. On striking the wall *X*, the molecules rebounds in reverse direction with the same speed u since the collision has been assumed to be perfectly elastic. The momentum of the molecule after it rebounds is $(-mu)$. Hence, the change in momentum of the molecules is

$$mu - (-mu) = 2mu$$

If the molecule travels with the velocity u to the wall opposite *ABCD* and rebounds back to *X* again without striking any other molecule on the way, it covers a distance $2l$ in time $\frac{2l}{u}$.

∴ The time interval between successive collisions of the molecules with the wall is $\frac{2l}{u}$.

By Newton's second law of motion the rate of change of momentum is equal to the impressed force.

∴ Rate of change of momentum at

$$\begin{aligned} \text{ABCD} &= \frac{\text{Change in momentum}}{\text{Time}} \\ &= \frac{2mu}{2l/u} = \frac{mu^2}{l} \end{aligned}$$

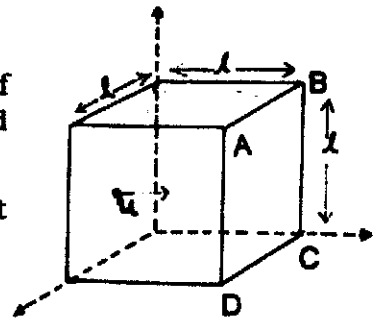


Fig. 11.1: Motion of a molecule, in a container

This is the rate of change of momentum due to one molecule. Since there are N molecules of the gas, therefore, the total rate of change of momentum or therefore the total force exerted on the wall *ABCD* due to impact of all the N molecules is

$$\text{Force on ABCD} = \frac{m}{l} (u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)$$

Where, $u_1, u_2, u_3, \dots, u_N$ are the velocity of first, second, third and ...: N^{th} molecule respectively along the *OX* direction.

We know that pressure = $\frac{\text{Force}}{\text{Area}}$

∴ the pressure P on the wall *X* of areas l^2 is given by

$$\begin{aligned} P &= \frac{\frac{m}{l} (u^2 + u_1^2 + u_2^2 + \dots + u_N^2)}{l^2} \\ P &= \frac{m}{l^3} (u^2 + u_1^2 + u_2^2 + \dots + u_N^2) \end{aligned} \quad \dots(11.1)$$

If \bar{u}^2 represents the mean value of the squares of all the speed components in the OX direction then

$$\bar{u}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2}{N}$$

or $N\bar{u}^2 = u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2$

Substituting the value of $(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2)$ in equation (11.1) we get

$$P = \frac{mN\bar{u}^2}{l^3} \quad \dots(11.2)$$

It can be shown by geometry that

$$c^2 = u^2 + v^2 + w^2$$

Since u , v and w are the components of c .

This relation also holds for the mean square values i.e.

$$\bar{c}^2 = \bar{u}^2 + \bar{v}^2 + \bar{w}^2$$

Since the molecules show no preference for moving parallel to any one edge of the cube; it follows that the mean value of u^2 , v^2 , w^2 are equal.

i.e. $\bar{u}^2 = \bar{v}^2 = \bar{w}^2$

$$\bar{c}^2 = 3\bar{u}^2$$

or $\bar{u}^2 = \frac{\bar{c}^2}{3}$

Substituting this in eqn. (11.2) we get

$$P = \frac{Nm\bar{c}^2}{3l^3}$$

But $l^3 =$ volume of the container = volume of the gas, V

$$\therefore PV = \frac{1}{3} Nm\bar{c}^2 \quad \dots(11.3)$$

This important relationship relates the macroscopic properties i.e. pressure and volume with the microscopic properties i.e. mass and mean square speed of the molecules.

Equation (11.3) can be re-written as,

$$P = \frac{1}{3} \frac{Nm}{V} \bar{c}^2$$

If ρ is the density of the gas, we can write

$$P = \frac{1}{3} \rho \bar{c}^2 \quad \left(\because \rho = \frac{mN}{V} \right)$$

or $\bar{c}^2 = \frac{3P}{\rho} \quad \dots(11.4)$

Note: The following points about the above derivation should be noted:

- (i) From equation (11.4) it is clear that in this expression the shape of the container does not play any role in kinetic theory. It is only the volume which is of significance. So instead of a cube we could have taken any other container. A cube only simplifies our calculations.
- (ii) We ignored the intermolecular collision but these would not have affected the result, because the average momentum of the molecules on striking the walls is unchanged by their collision with each other.
- (iii) The mean square speed \bar{c}^2 is not the same as the square of the mean speed. This is illustrated by the following examples.

Suppose we have five molecules and their speeds are 1, 2, 3, 4, 5 units respectively. Then their mean speed is

$$\frac{1+2+3+4+5}{5} = 3 \text{ units}$$

Its square is 9.

On the other hand the mean square speed is

$$\frac{1^2+2^2+3^2+4^2+5^2}{5} = \frac{55}{5} = 11$$

Thus we see that mean square speed which is 11 units in the above example is not the same as mean speed which is 3.

Example 11.1: Calculate the pressure exerted by 10^{22} molecules of oxygen each of mass 5×10^{-26} kg in a hollow cube of side 10 cm where the average translational speed of molecule is 500 ms^{-1} .

Solution: Change in momentum $= 2mu = 2 \times 5 \times 10^{-26} \times 500$
 $= 5 \times 10^{-22} \text{ kg ms}^{-1}$

Time taken to make successive impacts on same side = time to travel $2 \times 10 \text{ cm}$ or $2 \times 10^{-2} \text{ m}$,

$$\text{i.e. Time} = \frac{2 \times 10^{-2}}{500} = 4 \times 10^{-4} \text{ s}$$

$$\therefore \text{Rate of change of momentum} = \frac{5 \times 10^{-22}}{4 \times 10^{-4}} = 1.25 \times 10^{-19} \text{ N}$$

The force on the side due to one third molecules

$$= \frac{1}{3} \times 1.25 \times 10^{-19} \times 10^{22} \text{ N} \approx 400 \text{ N}$$

$$\text{and pressure} = \frac{\text{Force}}{\text{Area}} = \frac{400 \text{ N}}{100 \times 10^{-4} \text{ m}^2} = 4 \times 10^4 \text{ N m}^{-2}$$

-INTEXT QUESTIONS 11.1-

1. (i) A gas fills a container completely but not a liquid. Why is this?
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ii) Solids have more ordered structure than gases. Why?

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2. What is an ideal gas ?

.....

3. How is pressure related to density of molecules ?

.....

11.4 DEDUCTIONS OF GAS LAWS FROM KINETIC THEORY

i) Boyle's Law

We know that the pressure P exerted by a gas is given by

$$P = \frac{mN \bar{c}^2}{V}$$

or $PV = \frac{1}{3} mN \bar{c}^2$ But $mN =$ total mass M of gas

$$\therefore PV = \frac{1}{3} M \bar{c}^2 \quad \dots(11.5)$$

When the temperature of a given mass of the gas is constant, the mean square speed is constant. Thus both M and \bar{c}^2 on the right hand side of eqn. (11.5) are constant. Thus we can write,

$$PV = \text{Constant}$$

This is Boyle's Law, which states that **At constant temperature, the pressure of**

a gas is inversely proportional to the volume of the gas.

(ii) Charles's Law

From eqn. (11.5) we know that

$$PV = \frac{1}{3} M \bar{c}^2$$

$M \bar{c}^2$ varies as T varies. Therefore PV should also vary as T vary. This is Charles's Law

$$\text{i.e.} \quad PV \propto T \quad (11.6)$$

Charles's Law may be stated in two ways:

The volume of a gas at constant pressure is directly proportional to the temperature OR The Pressure of a gas at constant volume is directly proportional to the temperature.

iii) Avogadro's Law

Let us consider two different gases 1 and 2. Then from kinetic theory

$$P_1 V_1 = \frac{1}{3} m_1 N_1 \bar{c}_1^2$$

$$P_2 V_2 = \frac{1}{3} m_2 N_2 \bar{c}_2^2$$

If their pressure, volume and temperature are the same, then

$$P_1 = P_2$$

and $V_1 = V_2$

$$\therefore \frac{1}{3} m_1 N_1 \bar{c}_1^2 = \frac{1}{3} m_2 N_2 \bar{c}_2^2 \quad \dots(11.7)$$

Since the temperature is constant therefore their kinetic energies will be the same i.e.

$$\frac{1}{2} m_1 \bar{c}_1^2 = \frac{1}{2} m_2 \bar{c}_2^2 \quad \dots(11.8)$$

Dividing equations (11.7) and by (11.8) we get $N_1 = N_2$

Hence, Equal volume of ideal gases existing under the same conditions of temperature and pressure contain equal number of molecules. This statement is Avogadro's Law

iv) Dalton's Law of partial pressure

Suppose we have a number of gases or vapours having no chemical reaction with each other. Let their densities be $\rho_1, \rho_2, \rho_3, \dots$ and mean square speeds $\bar{c}_1^2, \bar{c}_2^2, \bar{c}_3^2, \dots$ respectively. We mix same volumes of these gases. Then the resultant pressure P is clearly given by

$$P = \frac{1}{3} \rho_1 \bar{c}_1^2 + \frac{1}{3} \rho_2 \bar{c}_2^2 + \frac{1}{3} \rho_3 \bar{c}_3^2 + \dots$$

Here, $\frac{1}{3} \rho_1 \bar{c}_1^2, \frac{1}{3} \rho_2 \bar{c}_2^2, \frac{1}{3} \rho_3 \bar{c}_3^2, \dots$ are the individual (or impartial) pressure of the different gases or vapours. If we denote these by p_1, p_2, p_3, \dots we get

$$P = p_1 + p_2 + p_3 + \dots$$

In other words : The total pressure exerted by the gaseous mixture is the sum of the individual pressures that would be exerted if several gases occupied the space in turn, alone. This is Dalton's law of partial pressure.

v) Graham's law of diffusion of gases

Graham investigated the diffusion of gases through porous substance and

found that; **The rate of diffusion of a gas through a porous partition is inversely proportional to the square root of its density. This is known as Graham's law of diffusion.**

On the basis of kinetic theory of gases, the rate of diffusion through a fine hole will be proportional to the average or root mean square velocity
 c. From equation (11.4a) we know that

$$\bar{c}^2 = \frac{3p}{P}$$

or

$$\bar{c} = \sqrt{\frac{3p}{P}}$$

(11.9)

∴ the root mean square velocity \bar{c}_1 and \bar{c}_2 of the molecules of two gas of densities ρ_1 and ρ_2 respectively at a pressure are

$$\bar{c}_1 = \sqrt{\frac{3p}{P_1}} \quad \text{and} \quad \bar{c}_2 = \sqrt{\frac{3p}{P_2}}$$

Thus,

$$\frac{\text{Rate of diffusion of one gas}}{\text{Rate of diffusion of other gas}} = \frac{\bar{c}_1}{\bar{c}_2} = \sqrt{\frac{P_2}{P_1}}$$

Thus,

$$\frac{\text{Rate of diffusion of one gas}}{\text{Rate of diffusion other gas}} = c$$

It thus follows that kinetic theory of gases provides a theoretical basis for Graham's law of diffusion of gases.

Example 11.2: What is the root mean square speed of hydrogen molecule at 300 K?

Mas of hydrogen molecule = $3.347 \times 10^{-27} \text{ kg} = m = 1.38 \times 10^{-27} \text{ JK}^{-1}$

Solution:

We know

$$c_{rms} = \sqrt{\frac{3kT}{m}} = \frac{3 \times (1.38 \times 10^{-27} \text{ JK}^{-1})(300\text{K})}{3.347 \times 10^{-27} \text{ Kg}}$$

$$= 1927 \text{ ms}^{-1}$$

Now, it is time to check Your understanding

INTEXT QUESTIONS 11.2

- Five gas molecules chosen at random are found to have speed of 500, 660, 700, 800 and 900 ms^{-1} . Find the RMS speed. Is it the same as the average speed?

2. If the same volumes of two gases 1 and 2 are mixed without any chemical reaction, then what would be the resultant pressure of the mixture?
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11.5 KINETIC INTERPRETATION OF TEMPERATURE

We know that the pressure of a gas is given by the relation

$$P = \frac{1}{3} \rho \bar{c}^2$$

$$\text{or } P = \frac{1}{3} \frac{mN\bar{c}^2}{V}$$

Multiplying by V , the volume of 1 gram molecule of the gas, we have

$$PV = \frac{1}{3} mN\bar{c}^2$$

Also for n mole of a gas, we have

$$PV = nRT \text{ where } R = \text{gas constant} = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$nRT = \frac{1}{3} mN\bar{c}^2$$

Multiplying both sides by $\frac{3}{2}$ we have

$$\frac{3}{2} RT = \frac{1}{2} \frac{mN\bar{c}^2}{n} = \frac{1}{2} mN_A \bar{c}^2$$

where $\frac{N}{n} = N_A$ Avogadro's number

$$\text{or } \frac{3(R)}{2 N_A} T = \frac{1}{2} m\bar{c}^2$$

11.4.1 Mean Kinetic Energy

But $\frac{1}{2} m\bar{c}^2$ is the mean kinetic energy of molecule. Therefore, mean kinetic energy of a molecule is

$$\frac{1}{2} m\bar{c}^2 = \frac{3}{2} \frac{R}{N_A} T$$

Here $\frac{R}{N_A}$ is a constant k , called Boltzman constant.

$$\text{i.e. } k = \frac{R}{N_A}$$

Avogadro's Number: The number of atoms or molecules in a mole of a substance is called Avogadro number. Its value is $6.023 \times 10^{23} \text{ mol}^{-1}$.

The value of $k = .38 \times 10^{-23} \text{ J molecule}^{-1} \text{ K}^{-1}$

\therefore mean kinetic energy of a molecule of the gas kT is given as

$$\frac{1}{2} m\bar{c}^2 = \frac{3}{2} kT \quad \dots(11.10)$$

Obviously, therefore, the kinetic energy of a gram-molecule of the gas

$$= \frac{3}{2} kN_A T = \frac{3}{2} \left(\frac{R}{N_A} \right) \times N_A T = \frac{3}{2} RT$$

Kinetic energy of a gram molecule of a gas $= \frac{3}{2} RT$

This relationship tells us that the kinetic energy of a molecule depends upon the absolute temperature T of the gas and it is quite independent of its mass. This fact is known as the **kinetic interpretation of temperature**.

Clearly, at $T = 0$ indicating that at the absolute zero of temperature, the kinetic energy of the gas is reduced to zero. In other words, all molecular motion ceases at this temperature, the molecule being all at rest.

From (11.10) we have the expression for the square root of \bar{c}^2 called root mean square velocity.

$$c_{rms} = \sqrt{\bar{c}^2} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

11.5.2. Pressure Temperature Relationship

From eqn. (11.5) we know that

$$PV = \frac{1}{3} M\bar{c}^2$$

From experimental evidence we know that for one gram-molecule of a gas the relation between pressure, volume and temperature is given by

$$PV = RT$$

where R = gas constant

...(11.11)

Combining equation (11.5) and (11.6) we get

$$\frac{1}{3} M\bar{c}^2 = RT$$

or

$$\bar{c}^2 = \frac{3R}{M} T \quad \dots(11.12)$$

But kinetic energy $= \frac{1}{2} M\bar{c}^2$.

So eqn (11.12) can be written as

$$\frac{2}{3} \times \frac{1}{2} M\bar{c}^2 = RT$$

or
$$\frac{1}{2} M\bar{c}^2 = \frac{3}{2} RT \quad \dots(11.13)$$

From this relation we see that the kinetic energy of one gram-molecule of the gas is equal to RT . From eqn. (11.12) we see that the mean-square velocity is directly proportional to the Kelvin Scale of temperature T .

At $T=0, \bar{c}^2 = 0$ or $c = 0$, hence we can define Kelvin zero as **The Kelvin zero on the kelvin scale of temperature is that temperature at which the molecular translational velocities of a gas are reduced to zero.**

In actual system the molecule may have the same energy for one molecule the Kinetic energy from eqn (11.13) can be written as

$$\frac{1}{2} M\bar{c}^2 = \frac{3}{2} \frac{R}{N_A} T$$

where $N_A =$ Avogadro's Number

But $\frac{R}{N_A} =$ Boltzman constant $= k$,

$$\therefore \frac{1}{2} M\bar{c}^2 = \frac{3}{2} kT$$

Thus, in a given mass of gas the mean kinetic energy per molecule is proportional to the temperature of the gas.

Example 11.3: At What temperature will the root mean square velocity of hydrogen be double of its value at S.T.P., pressure being constant (STP = Standard temperature and pressure).

Solution: We know that,

$$\frac{1}{2} M\bar{c}^2 = \frac{3}{2} RT$$

or $\bar{c}^2 \propto T$

or $\bar{c} \propto \sqrt{T}$

Let the velocity at N.T.P. i.e at T_0 K be \bar{c}_0 .

If T_0 K is the required temperature, the velocity c at the temperature $= 2\bar{c}_0$ as given in the problem

$$\frac{\bar{c}}{\bar{c}_0} = \frac{2\bar{c}_0}{\bar{c}_0} = \sqrt{\frac{T}{T_0}}$$

Taking square on both sides we get

$$4 = \frac{T}{T_0}$$

or $T = 4 T_0$

Since $T_0 = 273\text{K}$

$T = 4 \times 273 = 1092\text{ K}$

$T = 1092 - 273 = 819^\circ\text{ C.}$

Example 11.4 : Find the average kinetic energy of a gas at temperature of 300 K. Given $k = 1.38 \times 10^{-23}\text{ JK}^{-1}$.

Solution: We know that

$$\frac{1}{2} M\bar{c}^2 = \frac{3}{2} kT$$

Since $k = 1.38 \times 10^{-23}\text{ JK}^{-1}$

$T = 300\text{ K}$

$$\begin{aligned} \therefore \text{Average KE} &= \frac{3}{2} (1.38 \times 10^{-23}\text{ JK}^{-1})(300\text{ K}) \\ &= 6.21 \times 10^{-21}\text{ J} \end{aligned}$$

11.5.3. The law of equipartition of energy

There are 3 directions of motion (X, Y and Z axes) which are equally probable for the gas molecules. This implies that average value of the components of velocity c (i.e. u , v and w) along the three directions should be equal or for a molecule all the three directions are equivalent.

i.e. $\bar{u} = \bar{v} = \bar{w}$

or $\bar{u}^2 = \bar{v}^2 = \bar{w}^2 = \frac{1}{3} \bar{c}^2$

Since $c^2 = u^2 + v^2 + w^2$

$\bar{c}^2 = \bar{u}^2 + \bar{v}^2 + \bar{w}^2$

Multiplying throughout by $\frac{1}{2}m$, where m is the mass of a molecule we have

$$\frac{1}{2} m\bar{u}^2 = \frac{1}{2} m\bar{v}^2 = \frac{1}{2} m\bar{w}^2$$

But $\frac{1}{2} m\bar{u}^2 = E_x =$ total mean kinetic energy of a molecule along X axis

Therefore $E_x = E_y = E_z$

But, the total mean kinetic energy of a molecule is

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

Where, $k =$ Boltzmann constant, and $T =$ Absolute temperature

and since, $E = E_x + E_y + E_z$

$$\therefore E_x = E_y = E_z = \frac{1}{2} kT$$

Since three velocity components u , v and w correspond to the three degree of freedom of the molecule, we can conclude that.

Total kinetic energy of a dynamical system is equally divided among all its degrees of freedom and it is equal or $\frac{1}{2}kT$ per degree of freedom.

This is the **law of equipartition of energy** and was deduced by James Clark Maxwell. Let us apply this law for different types of gases.

So far we have been considering only translational motion. Let us now consider rotation too. Of course, for a **monoatomic molecule**, we have only translational motion because they are not capable of rotation (although they can spin about any one of the three mutually perpendicular axes if it is like a finite sphere). Hence for one molecule of a **monoatomic gas** total energy.

$$E = \frac{3}{2}kT. \quad (11.14)$$

For a **diatomic molecule** we can suppose it to be two spheres joined by a rigid rod. Such a molecule can rotate about any one of the three mutually perpendicular axes. However, the rotational inertia about an axis along the rigid rod is negligible compared to that about an axis perpendicular to the rod, so that rotational energy consists of two terms such as $\frac{1}{2}I\omega_y^2$ and $\frac{1}{2}I\omega_z^2$.

Now the special description of the centre of mass of a diatomic gas molecule will require three coordinates. Thus, for a diatomic gas molecule having both rotational and translational motion.

$$E = 3\left(\frac{1}{2}kT\right) + 2\left(\frac{1}{2}kT\right)$$

or $E = \frac{5}{2}kT \quad \dots(11.15)$

For **triatomic gases**, each molecule contains three spheres joined together by rods (we can suppose) so that the molecule is capable of rotating energetically about each of three mutually perpendicular axes. Hence for a triatomic gas molecule having both translational motion. energy E will be

$$E = 3\left(\frac{1}{2}kT\right) + 3\left(\frac{1}{2}kT\right)$$

or $E = 3kT \quad (11.16)$

(Here three degrees of freedom for the translation of the centre of mass of the molecule and three for rotation along three mutually perpendicular axes).

11.6 SPECIFIC HEATS OF GASES

We know that the temperature of a gas can be raised under different

conditions of volume and pressure. For example, the volume may be kept constant or the pressure may be kept constant or both may be allowed to vary in some arbitrary manner. In each of these cases the amount of heat required to cause unit rise of temperature in unit mass is different. Hence, a gas has different heat capacities.

If we supply an amount of heat Q to a gas to raise its temperature through T then heat capacity is defined as

$$\text{Heat capacity} = \frac{Q}{T} \quad (11.17)$$

The heat capacity of a body per unit mass of the body is called as **specific heat** of the substance of which the body is made and is usually denoted by C (or S). Thus

$$\text{Specific heat } C = \frac{\text{heat capacity}}{m} \quad (11.18)$$

Equations (11.17) & (11.18) gives

$$C = \frac{Q}{m \Delta T} \quad (11.19)$$

It may be defined as follows,

Specific heat of a material is the heat required to raise the temperature of unit mass of that material for unit temperature change.

The unit of specific heat in MKS system is kilo calories per kilogram per Kelvin ($\text{kcal kg}^{-1} \text{K}^{-1}$)

It may also be expressed in joules per kg per K. For example specific heat of water is

$$1 \text{ kilo cal kg}^{-1} \text{K}^{-1} = 4.2 \times 10^3 \text{ joule kg}^{-1} \text{K}^{-1}.$$

The above definition of specific heat holds good for solids and liquids and not for gases because according to relation (11.19) specific heat of a gas may vary from zero to infinity. To elaborate, if we compress a certain gas, there is a rise in temperature without supplying any heat to the gas from outside. Thus, we see that for mass m of a gas we have,

$$C = \frac{Q}{m \Delta T} = \frac{0}{m \times \Delta T}$$

Again, if we supply heat to a gas and the gas is allowed to expand such that there is no rise in temperature, i.e. $\Delta T = 0$ then,

$$C = \frac{Q}{m \times \Delta T} = \frac{0}{m \times \Delta T} = \alpha$$

We observe that in order to study the specific heat of a gas, either the pressure or the volume of the gas has to be kept constant.

Consequently, gases have two specific heats i.e.

- 1) Specific heat at constant volume denoted as C_v

ii) Specific heat at constant pressure denoted as C_p ,

The two specific heats are defined as follows:

(a) **The specific heat of a gas at constant volume (C_v)** is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1 K when its volume is kept constant.

$$\text{i.e.} \quad C_v = \left(\frac{\Delta Q}{\Delta T} \right), \quad \dots(11.20)$$

(b) **The specific heat at constant pressure (C_p)** is defined as the amount of heat required raise the temperature of unit mass of a gas through 1 K when its pressure is kept constant.

$$C_p = \left(\frac{\Delta Q}{\Delta T} \right), \quad \dots(11.21)$$

Note : When 1 mole of a gas is considered then the amount of heat required to raise the temperature by one degree is called **molar specific heat**.

We know that when pressure is kept constant, the volume of the gas increases. Hence in the second case note that the heat required to raise the temperature of unit mass through 1 degree at constant pressure is made up of two parts:

- i) heat required to do external work to produce a change in volume of the gas and
- ii) heat required to raise the temperature of the gas through one degree (C_v).

This means the specific heat of a gas at constant pressure is greater than its specific heat at constant volume by an amount which is the thermal equivalent of the work done in expanding the gas against external pressure. That is

$$C_p = W + C_v \quad \dots(11.22)$$

11.6.1. Relation between C_p and C_v

Let us consider one mole of an ideal gas enclosed in cylinder fitted with a frictionless movable piston (see Fig. 11.2) Since the gas has been assumed to be ideal (perfect), there is no intermolecular force between its molecules and when such a gas expands an internal work is done in separating the gas molecules apart. This whole work is only external i.e., against the internal pressure

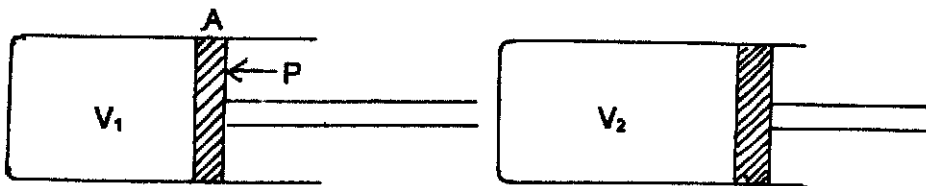


Fig. 11.2: Gas heated at constant pressure:

Let P be the external pressure and A be the cross sectional area of the piston.

The force acting on the piston = $P \times A$

Now, suppose the gas is heated at constant pressure through 1 K and as a result the piston moves outward through a distance X as shown in the figure 11.2. Let V_1 be the initial volume of the gas and V_2 be the volume after heating.

Therefore, the work W done by the gas in pushing the piston through the distance x , against external pressure P is given by

$$\begin{aligned}W &= P \times A \times x \\ &= P \times (\text{Increase in volume}) \\ &= P (V_2 - V_1)\end{aligned}$$

We know from (11.22) that $C_p + C_v = \text{Work done } (W) \text{ against the external pressure in raising the temperature of 1 mole of a gas through 1 K i.e.}$

$$C_p - C_v = P (V_2 - V_1) \quad \dots(11.23)$$

Now applying perfect gas equation to these two stages of the gas i.e before and after heating we have

$$PV_1 = RT \quad \dots(11.24)$$

$$PV_2 = R (T + 1) \quad \dots(11.25)$$

Subtracting (11.24) from (11.25) we get

$$P(V_2 - V_1) = R \quad \dots(11.26)$$

\therefore From (11.20) and (11.23) we get

$$C_p - C_v = R \quad \dots(11.27)$$

where R is in Joules mole⁻¹ K⁻¹

Converting Joules into Calories, we get

$$C_p - C_v = \frac{R}{J} \quad \dots(11.28)$$

where, $J = 4.18 \text{ J cal}$ is the mechanical equivalent of heat.

Example 11.5: Find out the value of C_p and C_v for a monoatomic, diatomic and triatomic gas molecules.

Solution: We know that the average KE for 1 mole for a gas is given as

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

Now C_v is defined as the heat required to raise the temperature of 1 mole of a gas at constant volume by one degree i.e. if

$$E_T = \text{Total energy of gas at } TK$$

$$E_{T+1} = \text{Total energy of gas at } (T + 1) K$$

Then $C_v = E_{T+1} - E_T$ (at constant volume)

(i) We know, for monoatomic gas, total energy = $\frac{3}{2} RT$

$$\begin{aligned} \therefore \text{for monoatomic gas } C_v &= \frac{3}{2}R(T+1) - \frac{3}{2}RT \\ &= \frac{3}{2}R. \end{aligned}$$

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

(ii) For diatomic gases, total energy = $\frac{5}{2}RT$

$$\begin{aligned} \therefore C_v &= \frac{5}{2}R(T+1) - R = \frac{5}{2}RT \\ C_p &= C_v + R = \frac{5}{2}R + R = \frac{7}{2}R. \end{aligned}$$

(iii) You may now find out C_v and C_p for triatomic gas.

INTEXT QUESTION 11.3

1. What is the total energy of nitrogen molecule?
.....
2. Calculate the value of C_p and C_v for nitrogen given, $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$.
.....
3. Why the gases have two types of specific heats?
.....

Some important constants

- Universal gas constant, $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$
- 1 atomic mass unit (a.m.u.) = $1.66 \times 10^{-27} \text{ kg}$
- Avogadro's number $N = 6.02 \times 10^{23}$ molecules per mole
- Boltzmann constant $K = 1.38 \times 10^{-23} \text{ molecule}^{-1} \text{ K}^{-1}$
- 1 standard atmosphere = 0.76 m of Hg
= $1.01 \times 10^5 \text{ Nm}^{-2}$
= $1.01 \times 10^5 \text{ pa}$

11.7 WHAT YOU HAVE LEARNT

- Kinetic theory assumes the existence of atoms and molecules of a gas and applies the law of mechanics to large number of them using averaging technique.
- Kinetic theory relates the macroscopic properties.

- Kinetic theory makes certain assumptions about the nature of molecules, their collisions and distribution in a gas.
- The pressure of gas is the average impacts per second of the molecules per units area or the walls of the container.
- Kinetic energy of a molecule depends upon the absolute temperature T and is independent of its mass.
- At absolute zero of temperature, the kinetic energy of a gas is reduced to zero. The molecular motion thus ceases at absolute zero of temperature.
- Gas laws can be derived on the basis of kinetic theory.
- The kelvin zero in the kelvin scale is that temperature at which the molecular translational velocities of a gas are reduced to zero.
- Depending on the volume and pressure, the amount of heat required to raise the unit temperature of unit mass of a gas is different. Hence there are two specific heats of gas.
 - i) Specific heat at constant volume (C_v)
 - ii) Specific, heat at constant pressure (C_p)
- When pressure remains constant for unit change in temperature, the volume increases. Hence the heat required to raise the unit temperature of unit mass of a gas at constant pressure consists of two parts:
 - i) heat required to do external work to produce a change in volume of the gas.
 - ii) heat required to raise the temperature of the gas through one degree
 i.e. $C_p = W + C_v$
 $C_p - C_v = \frac{R}{J}$
- The law of equipartition of energy states that the total kinetic energy of a dynamical system is equally divided among all its degrees of freedom and it is equal to $\frac{1}{2} kT$ per degree of freedom.
- Total energy for a molecule of
 - (i) a monoatomic gas $= \frac{3}{2} kT$
 - (ii) a diatomic gas $= \frac{5}{2} kT$
 - (iii) a triatomic gas $= 3 kT$.

11.8 TERMINAL QUESTIONS

1. Can we use Boyle's law to compare two different ideal gases?
2. What will be the velocity and kinetic energy of the molecules of a substance at absolute zero temperature?
3. If the absolute temperature of a gas be made four times, what will happen to its kinetic energy, root-mean square velocity and pressure/
4. What is the ratio of average velocities of hydrogen molecules (molecular mass 2) and oxygen molecules (molecular mass 32) in a mixture of two gases to have the same kinetic energy per molecule?

5. If three molecules have velocities 0.5, 1 and 2 km/s respectively, calculate the ratio of the root mean square and average speeds.
6. Explain what is meant by the root-mean square velocity of the molecules of gas. Use the concepts of kinetic theory of gases to derive an expression for the root-mean square velocity of the molecules in terms of pressure and density of the gas.
7. i) Calculate the average translational kinetic energy of a neon atom at 25° C.
 (ii) At what temperature does the average energy have half this value?
8. A container of volume of 50 cm³ contains hydrogen at pressure of 1.0 Pa and at a temperature of 27° C. Calculate
 - a) the number of molecules of the gas in the container and
 - b) their root-mean square speed.
 ($R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$, $N = 6.0 \times 10^{26} \text{ mol}^{-1}$, mass of 1 mole of hydrogen molecule = $20 \times 10^{-3} \text{ kg mol}^{-1}$).
9. A closed container contains hydrogen which exerts a pressure of 20.0 mm Hg at a temperature of 50 OK.
 - a) At what temperature will it exert pressure of 180 mm Hg?
 - b) If the root mean square velocity of the hydrogen molecules at 10. OK is 800 ms⁻¹, what will be their root-mean square velocity at this new temperature?
10. State the assumptions of kinetic theory of gases.
11. Find an expression for pressure of a gas.
12. Deduce Boyle's Law and Charlie's Law from Kinetic theory of gases.
13. What is the interpretation of temperature on the basis of kinetic theory of gases?
14. What is Avagadro's Law? How can it be deduced from kinetic theory of gases?
15. Calculate the root-mean square of the molecules of hydrogen at 0° C at 100° C. (Density of hydrogen at 0° C and 760 mm of mer cury pressure = 0.09 kg m⁻³).
16. Calculate the pressure in mm of mercury exerted by hydrogen gas if the number of molecules per m³ is 6.80×10^{24} and the root mean square speed of the molecules is $1.90 \times 10^3 \text{ ms}^{-1}$. Avogadro's no. 6.02×10^{23} and molecular weight of hydrogen = 2.02.
17. Define specific heat of gases at constant pressure. Derive the relationship between C_p and C_v .
18. Define specific heat of gases at constant volume. Prove that for a tiratomic gas $C_v = 3R$.
19. Calculate C_p and C_v for argon, given $R = 8.3 \text{ Jmol}^{-1}\text{K}^{-1}$

ANSWER TO INTEXT QUESTIONS

INTEXT QUESTION 11.1

1. (i) Because in a gas the cohesive force between the molecules are extremely small as compared to the molecules in a liquid.
 (ii) Because the molecules in a solid are closely packed. The bonds between the molecules are stronger giving a ordered structure.
2. The gas which follows the kinectic theory of molecules is called as an ideal gas.

3. $P = \frac{1}{3} \rho \bar{c}^2$

INTEXT QUESTION 11.2

1. Average speed $\bar{c} = \frac{500+600+700+800+900}{5}$
 $= 700 \text{ ms}^{-1}$

$$\text{Average value of } \bar{c}^2 = \frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5}$$

$$= 510,000 \text{ m}^2 \text{ s}^{-2}$$

$$c_{\text{rms}} = \sqrt{\bar{c}^2} = \sqrt{510,000} = 714 \text{ ms}^{-1}$$

c_{rms} and \bar{c} are not same

2. The resultant pressure of the mixture will be the sum of the pressure of gases 1 and 2 respectively
i.e. $P = P_1 + P_2$.

INTEXT QUESTION 11.3

- (1) For each degrees of freedom, energy = $\frac{1}{2}kT$

\therefore for 5 degrees of freedom for a molecule of nitrogen total energy = $\left[\frac{5}{2}kT \right]$.

- (2) C_v for a diatomic molecule = $\frac{5}{2}R$

$$\text{or } C_v = \frac{5}{2} \times 8.3 \text{ J mol}^{-1} \text{ K}^{-1} = 20.75 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$C_p = C_v + R = 29.05 \text{ J mol}^{-1} \text{ K}^{-1}$$

TERMINAL EXERCISE

- | | |
|---|--|
| (7) (i) $6.18 \times 10^{-21} \text{ J}$ | (ii) -12°C |
| (8) (a) 1.2×10^{16} | (b) $1.9 \times 10^3 \text{ ms}^{-1}$ |
| (9) (a) 450 K | (b) $2.40 \times 10^3 \text{ ms}^{-1}$ |
| (10) $840 \text{ m}^2 \text{ s}^{-1}, 2150 \text{ ms}^{-1}$ | |