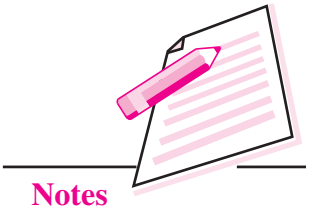



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10

# KINETIC THEORY OF GASES

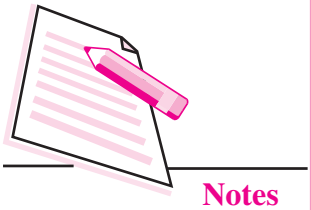
As you have studied in the previous lessons, at standard temperature and pressure, matter exists in three states – solid, liquid and gas. These are composed of atoms/ molecules which are held together by intermolecular forces. At room temperature, these atoms/molecules have finite thermal energy. If thermal energy increases, molecules begin to move more freely. This state of matter is said to be the gaseous state. In this state, intermolecular forces are very weak and very small compared to their kinetic energy.

Under different conditions of temperature, pressure and volume, gases exhibit different properties. For example, when the temperature of a gas is increased at constant volume, its pressure increases. In this lesson you will learn the kinetic theory of gases which is based on certain simplifying assumptions.You will also learn the kinetic interpretation of temperature and its relationship with the kinetic energy of the molecules. Why the gases have two types of heat capacities and concept of thermal expansion will also be explained in this lesson.

## OBJECTIVES

After studying this lesson, you should be able to :

- *define heat capacity and specific heat;*
- *state principle of caorimetry;*
- *explain thermal expansion;*
- *derive relation between* $\alpha$, $\beta$ *and* $\gamma$*;*
- *state the assumptions of kinetic theory of gases;*
- *derive the expression for pressure* $P = \frac{1}{3}\rho\overline{c^2}$ *;*
- *explain how rms velocity and average velocity are related to temperature;*
- *derive gas laws on the basis of kinetic theory of gases;*



Notes



- *give kinetic interpretation of temperature and compute the mean kinetic energy of a gas;*
- *explain degrees of freedom of a system of particles;*
- *explain the law of equipartition of energy;*
- *explain why a gas has two heat capacities; and*
- *derive the relation* $c_p - c_V = R/J$.

## 10.1 THERMAL ENERGY

During a year, the spring (Basant) season, when the temperature is not as high as in summer and not as low as in winter, is very pleasant. How does this change in temperature affect our day to day activities? How do things change their properties with change in temperature? Is there any difference between temperature and heat? All such questions will be discussed in the following sections.

The term temperature and heat are often used interchangeably in everyday language. In Physics, however, these two terms have very different meaning. Supply of heat does often increase the temperature but does it happen so when water boils or freezes? Why the wind in the coastal areas often reverses direction after the Sun goes down? Why does ice melt when kept on the palm of hand and why does the palm feel cool? All these facts will be explained in this chapter.

### 10.1.1 Heat Capacity and Specific Heat

When heat is supplied to a solid (or liquid), its temperature increases. The rise in temperature is found to be different in different solids in spite of having the same mass and being supplied the same quantity of heat. This simply implies that the rise in the temperature of a solid, when a certain amount of heat is supplied to it, depends upon the nature of the material of the solid. The nature of the solid is characterized by the term specific heat capacity or specific heat of the solid. The specific heat of the material of a solid (or a liquid) may be defined as the amount of heat required to raise the temperature of its unit mass through 1°C or 1K.

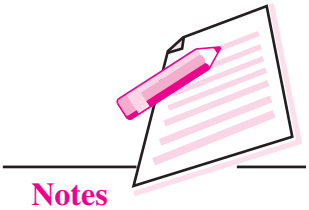
If an amount of heat $\Delta Q$ is required to raise the temperature of a mass $m$ of the solid (or liquid) through $\Delta\theta$, then the specific heat may be expressed as

$$C = \frac{\Delta Q}{m\Delta\theta}$$

Thus, the amount of heat required to raise the temperature of a substance is given by:

$$\Delta Q = mC\Delta\theta$$

SI unit of specific heat is J $kg^{-1}$ $K^{-1}$





### 10.1.2 Calorimetry

When two bodies at different temperatures are kept in contact, transfer of heat takes place from the body at higher temperature to the body at lower temperature till both the bodies acquire the same temperature. The specific heat of a material and other physical quanties related to this heat transfer are measured with the help of a device called calorimeter and the process of the measurement is called calcorimetry.

### 10.1.3 Principle of Calorimetry

Let two substances of mass $m_1$ and $m_2$, of specific heat capacities $C_1$ and $C_2$ and at temperatures $\theta_1$ and $\theta_2(\theta_1 > \theta_2)$, respectively be kept in contact. Then, the heat will be transferred from the higher to the lower temperature and the substances will acquire the same temperature $\theta$. (say) assuming that no energy loss takes place to the surroundings and applying the law of conservation of energy, we can say

$$\text{Heat lost} = \text{Heat gained.}$$

$$\Rightarrow \quad m_1C_1(\theta_1 - \theta) = m_2C_2(\theta - \theta_2)$$

This is the principle of calorimetry. By using this relation the resultant temperature $\theta$ can be determined. Also, by knowing $\theta_1$, $\theta_2$ and $\theta$ the specific heat capacity of a substance can be determined if the specific heat capacity of the other substance is known.

### 10.1.4 Thermal Expansion

When heat is given to a substance it expands in length, area or volume. This is called thermal expansion. The expansion in length, area and volume are called linear, superficial and cubical expansion, respectively.

In linear expansion, the change in length is directly proportional to the original length and change in temperature.

$$\Delta l \propto l_0 \Delta\theta$$

or

$$\Delta l = \alpha\, l_0 \Delta\theta$$

where $\alpha$ is the coefficient of linear expansion or temperature coefficient of linear expansion. It is given by

$$\alpha = \frac{\Delta l}{l_0 \Delta\theta}$$

If, $\Delta\theta = 1°C$ and $l_0$ = 1m

Then $\alpha = \Delta l$

Thus, $\alpha$ is defined as the change in length of unit length of the substance whose temperature is increased by 1°C.

In superficial expansion, the change in area is directly proportional to the original area and change in temperature:

$$\Delta A \propto A_0 \Delta\theta$$

or $$\Delta A = \beta A_0 \Delta\theta$$

where $\beta$ is the temperature coefficient of superficial expansion.

In cubical expansion, the change in volume is directly proportional to the change in temperature and original volume:

$$\Delta V \propto V_0 \Delta\theta$$

or $$\Delta V = \gamma V_0 \Delta\theta$$

where $\gamma$ in the temperature coefficient of cubical expansion.

If $V_0 = 1m^3$ and $\Delta\theta = 1°C$, then $\gamma = \Delta V$

Thus, coefficient of cubical expansion is defined as the change in volume of a unit volume of a substance whose temperature is increased by 1°C.

**Relation between $\alpha$, $\beta$ and $\gamma$**

Let there be a cube of side l whose temperature is increased by 1°C.

The change in length:

$$\Delta l = \alpha l \Delta\theta$$

$$= \alpha l \qquad (\because \Delta\theta = l°C)$$

or, new length $l' = l + \Delta l = l + \alpha l = l(1+\alpha)$

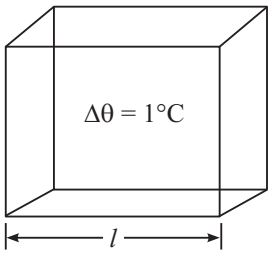
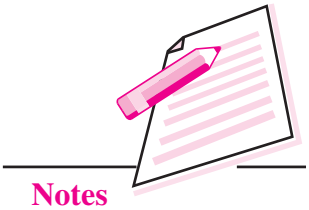



**Fig. 10.1**





Thus, $$\alpha = \frac{\Delta l}{l}$$

And $$\beta = \frac{\Delta A}{A} = \frac{l^2(1+\alpha)^2 - l^2}{l^2}$$

$$= 1 + \alpha^2 + 2\alpha - 1$$

Since $\alpha$ is very small therefore $\alpha^2$ may be neglected. We therefore have

$$\beta = 2\alpha$$

similarly, $$\gamma = \frac{\Delta V}{V} = \frac{l^3(1+\alpha)^3 - l^3}{l^3}$$

or, $$\gamma = l^3 + \alpha^3 + 3\alpha^2 + 3\alpha - l^3$$

As $\alpha$ is very small, the term $\alpha^2$ and $\alpha^3$ may be neglected. We , therefore, have

$\therefore$ $$\gamma = 3\alpha.$$

### 10.1.5 Anomalous expansion in water and its effect

Generally, the volume of a liquid increases with increase in temperature. The coefficient of expansion of liquids is about 10 times that of solids. However the volume of water does not increase with temperature between 0 to 4°C.

As the temperature increases from 0°C to 4°C, the water contracts and hence the density of water reaches a maximum value of 1 g $mL^{-1}$ or 1000 kg $m^{-3}$ at 4°C. After that the volume starts increasing (while the density decreases) as shown in Fig. 10.2.

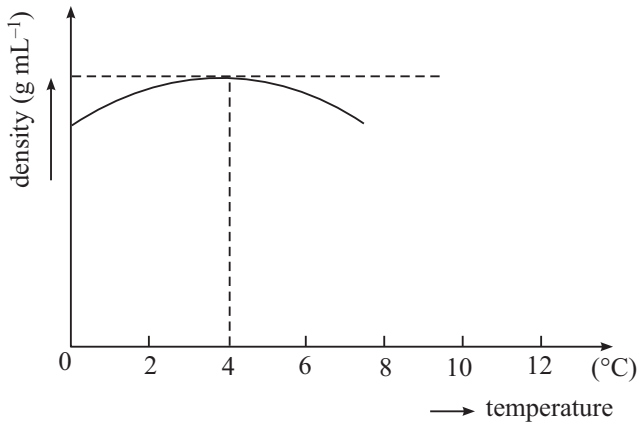



Fig. 10.2

Notes



Now, it can be understood why a pond or lake freezes at its surface whereas water may remain below it in liquid state. As the pond cools, the colder, denser water at the surface initially sinks to the bottom. When the temperature of the entire water body reaches 4°C, this flow stops. The temperating of surface water keeps on decreasing and freezes ultimately at 0°C. As water freezes at the surface, it remains there since ice is a bad conductor of heat; and since ice is less denser than water the ice continues to build up at the surface whereas water near the bottom remains at 4°C. If this had not happened fish and all the marine life would not have survived.

### 10.1.6 Thermal Expansion in Gases

When heat is supplied to the gases they also expand. This expansion is very large as compared to solids and liquids. But in case of a gas pressure and volume both may change simultaneously with rise in temperature. Hence we have to consider either expansion of the gas with temperature at constant pressure or the increase in its pressure at constant volume. Thus the coefficient of volume expansion of a gas at constant pressure is given by

$$\gamma_v = \left( \frac{V_2 - V_1}{V_1 \Delta\theta} \right)_{\Delta p=0}$$

and similarly

$$\gamma_p = \left( \frac{p_2 - p_1}{p_1 \Delta\theta} \right)_{\Delta v=0}$$

## 10.2 KINETIC THEORY OF GASES

You now know that matter is composed of very large number of atoms and molecules. Each of these molecules shows the characteristic properties of the substance of which it is a part. Kinetic theory of gases attempts to relate the macroscopic or bulk properties such as pressure, volume and temperature of an ideal gas with its microscopic properties such as speed and mass of its individual molecules. The kinetic theory is based on certain assumptions. (A gas whose molecules can be treated as point masses and there is no intermolecular force between them is said to be ideal.) A gas at room temperature and atmospheric pressure (low pressure) behaves like an ideal gas.

### 10.2.1 Assumptions of Kinetic Theory of Gases

Clark Maxwell in 1860 showed that the observed properties of a gas can be explained on the basis of certain assumptions about the nature of molecules, their motion and interaction between them. These resulted in considerable simplification. We now state these.

(i) A gas consists of a very large number of identical rigid molecules, which move with all possible velocities randomly. The intermolecular forces between them are negligible.

(ii) Gas molecules collide with each other and with the walls of the container. These collisions are perfectly elastic.

(iii) Size of the molecules is negligible compared to the separation between them.

(iv) Between collisions, molecules move in straight lines with uniform velocities.

(v) Time taken in a collision is negligible as compared to the time taken by a molecule between two successive collisions.

(vi) Distribution of molecules is uniform throughout the container.

To derive an expression for the pressure exerted by a gas on the walls of the container, we consider the motion of only one molecule because all molecules are identical (Assumption i). Moreover, since a molecule moving in space will have velocity components along $x$, $y$ and $z$–directions, in view of assumption (vi)it is enough for us to consider the motion only along one dimension, say $x$-axis.(Fig. 10.1). Note that if there were $N$ ($= 6 \times 10^{26}$ molecules $m^{-3}$), instead of considering $3N$ paths, the assumptions have reduced the roblem to only one molecule in one dimension. Let us consider a molecule having velocity $C$ in the face LMNO. Its $x$, $y$ and z components are u, v and w, respectively. If the mass of the molecule is $m$ and it is moving with a speed $u$ *along* $x$*–axis*, its momentum will be $mu$ towards the wall and normal to it. On striking the wall, this molecule will rebound in the opposite direction with the same speed $u$, since the collision has been assumed to be perfectly elastic (Assumption ii). The momentum of the molecule after it rebounds is $(-mu)$. Hence, the change in momentum of a molecule is

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

If the molecule travels from face LMNO to the face ABCD with speed $u$ along $x$–*axis* and rebounds back without striking any other molecule on the way, it covers a distance $2l$ in time $2l/u$. That is, the time interval between two successive collisions of the molecules with the wall is $2l/u$.

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

$$\text{Rate of change of momentum at ABCD} = \frac{\text{Change in momentum}}{\text{Time}}$$

$$= \frac{2mu}{2l/u} = \frac{mu^2}{l}$$

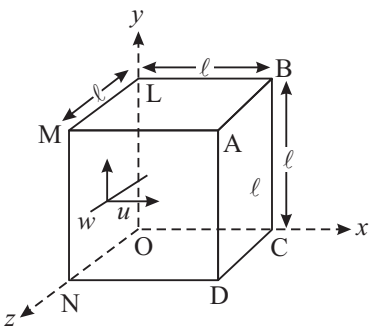



**Fig. 10.3 :** Motion of a molecule in a container

This is the rate of change of momentum of one molecule. Since there are $N$ molecules of the gas, the total rate of change of momentum or the total force exerted on the wall ABCD due to the impact of all the $N$ molecules moving along $x$-axis with speeds, $u_1, u_2, ..., u_N$ is given by

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

We know that pressure is force per unit area. Therefore, the pressure P exerted on the wall ABCD of areas $l^2$ by the molecules moving along $x$-axis is given by

$$P = \frac{\frac{m}{l}\left(u_1^2 + u_2^2 + \ldots + u_N^2\right)}{l^2}$$

$$= \frac{m}{l^3}\left(u_1^2 + u_2^2 + \ldots + u_N^2\right) \qquad (10.1)$$

If $\overline{u}^2$ represents the mean value of the squares of all the speed components along $x$-axis, we can write

$$\overline{u}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \ldots + u_N^2}{N}$$

or $$N\overline{u}^2 = u_1^2 + u_2^2 + u_3^2 + \ldots + u_N^2$$

Substituting this result in Eqn. (10.1), we get

$$P = \frac{Nm\overline{u^2}}{\ell^3} \qquad (10.2)$$

It can be shown by geometry that

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

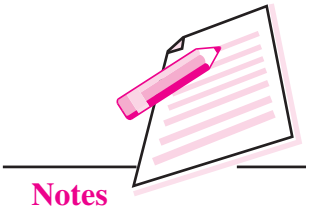
since $u$, $v$ and $w$ are components of $c$ along the three orthogonal axes. This relation also holds for the mean square values, i.e.

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

Since the molecular distribution has been assumed to be isotropic, there is no preferential motion along any one edge of the cube. This means that the mean value of $u^2$, $v^2$, $w^2$ are equal :

$$\overline{u}^2 = \overline{v^2} = \overline{w}^2$$

so that $$\overline{u}^2 = \frac{\overline{c}^2}{3}$$





Substituting this result in Eqn. (10.2), we get

$$P = \frac{1}{3}\frac{Nm}{\ell^3}\overline{c^2}$$

But $l^3$ defines the volume V of the container or the volume of the gas. Hence, we get

$$PV = \frac{1}{3}Nm\overline{c^2} = \frac{1}{3}M\overline{c^2} \qquad (10.3)$$

Note that the left hand side has macroscopic properties i.e. pressure and volume and the right hand side has only microscopic properties i.e. mass and mean square speed of the molecules.

Eqn (10.3) can be re-written as

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

If $\rho = \frac{mN}{V}$ is the density of the gas, we can write

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

or

$$\overline{c^2} = \frac{3P}{\rho} \qquad (10.4)$$

If we denote the ratio $N/V$ by number density $n$, Eqn. (10.3) can also be expressed as

$$P = \frac{1}{3}mn\overline{c^2} \qquad (10.5)$$

The following points about the above derivation should be noted:

(i) *From Eqn.* (10.4) *it is clear that the shape of the container does not play any role in kinetic theory; only volume is of significance. Instead of a cube we could have taken any other container. A cube only simplifies our calculations.*

*(ii) We ignored the intermolecular collisions but these would not have affected the result, because, the average momentum of the molecules on striking the walls is unchanged by their collision; same is the cose when they collide with each other.*

*(iii) The mean square speed* $\overline{c^2}$ *is not the same as the square of the mean speed.* This is illustrated by the following example.

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 (nine).

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 is not the same as square of mean speed.

**Example 10.1 :** Calculate the pressure exerted by $10^{22}$ molecules of oxygen, each of mass $5 \times 10^{-26}$ kg, in a hollow cube of side 10 cm where the average translational speed of molecule is 500 m $s^{-1}$.

**Solution :** Change in momentum $2mu = 2 \times (5 \times 10^{-26} \text{ kg}) \times (500 \text{ m s}^{-1})$

$$= 5 \times 10^{-23} \text{ kg m s}^{-1}.$$

Time taken to make successive impacts on the same face is equal to the time spent in travelling a distance of $2 \times 10$ cm or $2 \times 10^{-1}$ m. Hence

$$\text{Time} = \frac{2 \times 10^{-2} \text{ m}}{500 \text{ ms}^{-1}} = 4 \times 10^{-4} \text{ s}$$

$$\therefore \text{ Rate of change of momentum} = \frac{5 \times 10^{-23} \text{ kg ms}^{-1}}{4 \times 10^{-4} \text{ s}} = 1.25 \times 10^{-19} \text{ N}$$

The force on the side due to one third molecules

and $$f = \frac{1}{3} \times 1.25 \times 10^{-19} \times 10^{22} = 416.7 \text{ N}$$

$$\text{pressure} = \frac{\text{Force}}{\text{Area}} = \frac{417 \text{ N}}{100 \times 10^{-4} \text{ m}^2}$$

$$= 4.2 \times 10^{-4} \text{ N m}^{-2}$$

## INTEXT QUESTIONS 10.1

1. (i) A gas fills a container of any size but a liquid does not. Why?
   (ii) Solids have more ordered structure than gases. Why?
2. What is an ideal gas?
3. How is pressure related to density of molecules?

4. What is meant by specific heat of a substance?
5. Define coefficient of cubical expansion.
6. A steel wire has a length of 2 m at 20°C. Its length becomes 2.01 m at 120°C. Calculate coefficient of linear expansion $\alpha$ of the material of wire.

## 10.3 KINETIC INTERPRETATION OF TEMPERATURE

From Eqn. (10.3) we recall that

$$P\,V = \frac{1}{3} m N \overline{c^2}$$

Also, for $n$ moles of a gas, the equation of state is $PV = n\,RT$, where gas constant $R$ is equal to 8.3 J mol$^{-1}$ K$^{-1}$. On combining this result with the expression for pressure, we get

$$n\,R\,T = \frac{1}{3} m N \overline{c^2}$$

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

$$\frac{3}{2} R\,T = \frac{1}{2} \frac{N m \overline{c^2}}{n} = \frac{1}{2} m\,N_A\,\overline{c^2}$$

where $\frac{N}{n} = N_A$ is Avogadro's number. It denotes the number of atoms or molecules in one mole of a substance. Its value is $6.023 \times 10^{23}$ per gram mole. In terms of $N_A$, we can write

$$\frac{3}{2}\left(\frac{R}{N_A}\right) T = \frac{1}{2} m \overline{c^2}$$

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

$$\frac{1}{2} m\,\overline{c^2} = \frac{3}{2}\left(\frac{R}{N_A}\right) T = \frac{3}{2} k\,T \qquad (10.6)$$

where

$$k = \frac{R}{N_A} \qquad (10.7)$$

is ***Boltzmann constant.*** The value of $k$ is $1.38 \times 10^{-23}$ J K$^{-1}$.

In terms of k, the mean kinetic energy of a molecule of the gas is given as

$$\overline{\varepsilon} = \frac{1}{2} m\,\overline{c^2} = \frac{3}{2} k\,T \qquad (10.8)$$

Hence, kinetic energy of a gram mole of a gas is $\frac{3}{2}$ R T

This relationship tells us that the kinetic energy of a molecule depends only on 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, the gas has no kinetic energy. In other words, all molecular motion ceases to exist at absolute zero and the molecules behave as if they are frozen in space. According to modern concepts, the energy of the system of electrons is not zero even at the absolute zero. The energy at absolute zero is known as *zero point energy*.

From Eqn.(10.5), we can write the expression for the square root of $\overline{c}^2$, called **root mean square speed :**

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

This expression shows that at any temperature T, the $c_{rms}$ is inversely proportional to the square root of molar mass. It means that lighter molecule, on an average, move faster than heavier molecules. For example, the molar mass of oxygen is 16 times the molar mass of hydrogen. So according to kinetic theory, the hydrogen molecules should move 4 times faster then oxygen molecules. It is for this reason that lighter gases are in the above part of our atmosphere. This observed fact provided an early important evidence for the validity of kinetic theory.

## 10.4 DEDUCTION OF GAS LAWS FROM KINETIC THEORY

### (i) Boyle's Law

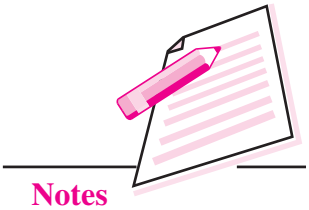
We know that the pressure P exerted by a gas is given by Eqn. (11.3) :

$$P V = \frac{1}{3} M \overline{c}^2$$

When the temperature of a given mass of the gas is constant, the mean square speed is constant. Thus, both $M$ and $\overline{c}^2$ on the right hand side of Eqn. (10.3) are constant. Thus, we can write

$$P V = \text{Constant} \qquad (10.9)$$

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





### (ii) Charle's Law

From Eqn. (10.3) we know that

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

or
$$V = \frac{1}{3} \frac{M}{P} \overline{c^2}$$

i.e, $V \propto \overline{c^2}$, if $M$ and P do not vary or $M$ and P are constant. But $\overline{c^2} \propto T$

$$\therefore \quad V \propto T \qquad (10.10)$$

***This is Charle's law : The volume of a given mass of a gas at constant pressure is directly proportional to temperature.***

**Robert Boyle**
**(1627 – 1691)**

British experimentalist Robert Boyle is famous for his law relating the pressure and volume of a gas (PV = constant). Using a vacuum pump designed by Robert Hook, he demonstrated that sound does not travel in vacuum. He proved that air was required for burning and studied the elastic properties of air.

A founding fellow of Royal Society of London, Robert Boyle remained a bachalor throughout his life to pursue his scientific interests. Crater Boyle on the moon is named in his honour.

**(iii) Gay Lussac's Law –** According to kinetic theory of gases, for an ideal gas

$$P = \frac{1}{3} \frac{M}{V} \overline{c^2}$$

For a given mass ($M$ constant) and at constant volume (V constant),

$$P \propto \overline{c^2}$$

But
$$\overline{c^2} \propto T$$

$$\therefore \quad P \propto T \qquad (10.11)$$

which is Gay Lussac's law. It states that **the pressure of a given mass of a gas is directly proportional to its absolute temperature T, if its volume remains constant.**

### (iv) Avogadro's Law

Let us consider two different gases 1 and 2. Then from Eqn. (10.3), we recall that

$$P_1 V_1 = \frac{1}{3} m_1 N_1 \overline{c_1^2}$$

and $$P_2V_2 = \frac{1}{3} m_2 N_2 \overline{c_2^2}$$

If their pressure and volume are the same, we can write

$$P_1V_2 = P_2V_2$$

Hence $$\frac{1}{3} m_1 N_1 \overline{c_1^2} = \frac{1}{3} m_2 N_2 \overline{c_2^2}$$

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

$$\frac{1}{2} m_1 \overline{c_1^2} = \frac{1}{2} m_2 \overline{c_2^2}$$

Using this result in the above expression, we get $N_1 = N_2$. (10.12)

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

### (v) Dalton's Law of Partial Pressure

Suppose we have a number of gases or vapours, which do not react chemically. Let their densities be $\rho_1, \rho_2, \rho_3$ ... and mean square speeds $\overline{c_1^2}$, $\overline{c_2^2}$, $\overline{c_3^2}$ ... respectively. We put these gases in the same enclosure. They all will have the same volume. Then the resultant pressure P will be given by

$$P = \frac{1}{3}\rho_1 \overline{c_1^2} + \frac{1}{3}\rho_2 \overline{c_2^2} + \frac{1}{3}\rho_3 \overline{c_3^2} + ...$$

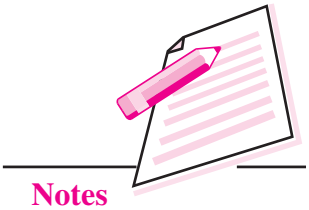
Here $\frac{1}{3}\rho_1 \overline{c_1^2}$, $\frac{1}{3}\rho_2 \overline{c_2^2}$, $\frac{1}{3}\rho_3 \overline{c_3^2}$ ... signify individual (or partial) pressures of different gases or vapours. If we denote these by $P_1$, $P_2$, $P_3$, respectively we get

$$P = P_1 + P_2 + P_3 + .... \quad (10.13)$$

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

### (vi) Graham's law of diffusion of gases

Graham investigated the diffusion of gases through porous substances 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 $c_{rms}$. From Eqn. (10.4) we recall that

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

or $$\sqrt{\overline{c^2}} = c_{rms} = \sqrt{\frac{3P}{\rho}}$$

That is, the root mean square velocities of the molecules of two gases of densities $\rho_1$ and $\rho_2$ respectively at a pressure P are given by

$$(c_{rms})_1 = \sqrt{\frac{3P}{\rho_1}} \quad \text{and} \quad (c_{rms})_2 = \sqrt{\frac{3P}{\rho_2}}$$

Thus,

$$\frac{\text{Rate of diffusion of one gas}}{\text{Rate of diffusion of other gas}} = \frac{(c_{rms})_1}{(c_{rms})_2} = \sqrt{\frac{\rho_2}{\rho_1}} \qquad (10.14)$$

Thus, rate of diffusion of gases is inversely proportional to the square root of their densities at the same pressure, which is Graham's law of diffusion.

**Example 10.2 :** Calculate the root mean square speed of hydrogen molecules at 300 K. Take m($H_2$) as $3.347 \times 10^{-27}$ kg and k = $1.38 \times 10^{-23}$ J mol$^{-1}$ K$^{-1}$

**Solution :** We know that

$$c_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3\times(1.38\times10^{-23}\text{ J K}^{-1})\,(300\text{ K})}{3.347\times10^{-27}\text{ kg}}}$$

$$= 1927 \text{ m s}^{-1}$$

**Example 10.3 :** 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 :** From Eqn. (10.8), we recall that

$$c_{rms} \propto \sqrt{T}$$

Let the rms velocity at S.T.P. be $c_0$.

If T K is the required temperature, the velocity $c = 2\ c_0$ as given in the problem

$$\therefore \quad \frac{c}{c_0} = \frac{2c_0}{c_0} = \sqrt{\frac{T}{T_0}}$$

Squaring both sides, we get

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

or $$T = 4T_0$$

Since $T_0 = 273K$, we get

$$T = 4\times273K = 1092K = 819^0C$$

**Example 10.4 :** Calculate the average kinetic energy of a gas at 300 K. Given k $= 1.38 \times 10^{-23}\,JK^{-1}$.

**Solution :** We know that

$$\frac{1}{2}M\,\bar{c}^2 = \frac{3}{2}k\,T$$

Since $k = 1.38 \times 10^{-23}\ J\ K^{-1}$ and $T = 300\ K$, we get

$$\therefore \quad \bar{E} = \frac{3}{2}\,(1.38 \times 10^{-23}\ J\ K^{-1})\ (300\ K)$$

$$= 6.21 \times 10^{-21}\ J$$

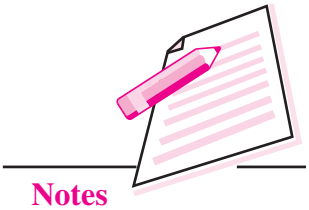
## INTEXT QUESTIONS 10.2

1. Five gas molecules chosen at random are found to have speeds 500 m $s^{-1}$, 600 m $s^{-1}$, 700 m $s^{-1}$, 800 m $s^{-1}$, and 900 m $s^{-1}$. Calculate their RMS speed.
2. If equal volumes of two non–reactive gases are mixed, what would be the resultant pressure of the mixture?
3. When we blow air in a balloon, its volume increases and the pressure inside is also more than when air was not blown in. Does this situation contradict Boyle's law?

### 10.4.1 Degrees of Freedom

Degrees of freedom of a system of particles are the number of independent ways in which the particles of the system can move.

Suppose you are driving along a road and several other roads are emanating from it towards left and right. You have the freedom to be on that road or to turn to the left or to the right you have two degrees of freedom. Now, say the





road has a flyover at some point and you take the flyover route. Now, you do not have any freedom to turn left or right, which means that your freedom has get restricted. You can move only along the flyover and we say that your degree of freedom is '1'.

Refer to Fig. 10.4. A string is tied in a taut manner from one end A to other end B between two opposite walls of a room. An ant is moving on it. Then its degree of freedom is '1'.

**Fig. 10.4**

Now suppose it falls on the floor of the room. Now, it can move along $x$ or $y$ direction independently. Hence its degrees of freedom is two. And if the ant has wings so that it can fly. Then it can move along $x$, $y$ or $z$ direction independently and its degree of freedom is '3'.

A monatomic molecule is a single point in space and like the winged ant in the above example has 3 degrees of freedom which are all translational. A diatomic molecule which is made up of two atoms, in addition to translator $y$ motion can also rotate about two mutually perpendicular axes. Hence a diatomic molecule has (3 + 2 = 5) degrees of freedom: three translational and two rotational.

## 10.5 THE LAW OF EQUIPARTITION OF ENERGY

We now know that kinetic energy of a molecule of a gas is given by $\frac{1}{2}m\bar{c^2} = \frac{3}{2}kT$.

Since the motion of a molecule can be along $x$, $y$, and $z$ directions equally probably, the average value of the components of velocity $c$ (i.e., $u$, $v$ and $w$) along the three directions should be equal. That is to say, for a molecule all the three directions are equivalent :

$$\bar{u} = \bar{v} = \bar{w}$$

and

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

Since

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

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

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 $\frac{1}{2}m\,\bar{u}^2 = E$ = 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 $\frac{3}{2}kT$. Hence, we get an important result :

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

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 to $\frac{1}{2}k$ T for each degree of freedom. This is the law of equipartition of energy and was deduced by Ludwing Boltzmann. Let us apply this law for different types of gases.

So far we have been considering only translational motion. 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

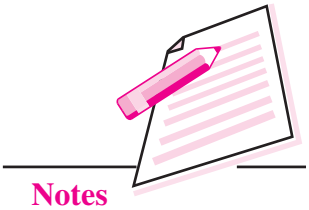
$$E = \frac{3}{2}kT \qquad (10.15)$$

A ***diatomic molecule*** can be visualised as if two spheres are 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. It means 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 molecules will require three coordinates. Thus, for a diatomic gas molecule, both rotational and translational motion are present but it has 5 degrees of freedom. Hence

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

$$= \frac{5}{2}kT \qquad (10.16)$$





**Ludwing Boltzmann**
**(1844 – 1906)**

Born and brought up in Vienna (Austria), Boltzmann completed his doctorate under the supervision of Josef Stefan in 1866. He also worked with Bunsen, Kirchhoff and Helmholtz. A very emotional person, he tried to commit suicide twice in his life and succeeded in his second attempt. The cause behind these attempts, people say, were his differences with Mach and Ostwald.

He is famous for his contributions to kinetic theory of gases, statistical mechanics and thermodynamics. Crater Bolzmann on moon is named in his memory and honour.

## 10.6 HEAT CAPACITIES OF GASES

We know that the temperature of a gas can be raised under different conditions of volume and pressure. For example, the volume 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 thermal energy required to increase unit rise of temperature in unit mass is different. Hence, we say that a gas has two different heat capacities.

If we supply an amount of heat $\Delta Q$ to a gas to raise its temperature through $\Delta T$, the heat capacity is defined as

$$\text{Heat capacity} = \frac{\Delta Q}{\Delta T}$$

The heat capacity of a body per unit mass of the body is termed as ***specific heat capacity*** of the substance and is usually denoted by c. Thus

$$\text{Specific heat capacity, } c = \frac{\text{heat capacity}}{m} \qquad (10.17)$$

Eqns. (10.16) and (10.17) may be combined to get

$$c = \frac{\Delta Q}{m\,\Delta T} \qquad (10.18)$$

***Thus, specific heat capacity of a material is the heat required to raise the temperature of its unit mass by* 1 °C *(or* 1 K*).***

The SI unit of specific heat capacity is kilo calories per kilogram per kelvin (kcal $kg^{-1}K^{-1}$). It may also the expressed in joules per kg per K. For example the specific heat capacity of water is

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

The above definition of specific heat capacity holds good for solids and liquids but not for gases, because it can vary with external conditions. In order to study the heat capacity of a gas, we keep the pressure or the volume of a gas constant. Consequently, we define two specific heat capacities :

(i) Specific heat at constant volume, denoted as $c_V$.

(ii) Specific heat at constant pressure, denoted as $c_P$.

(a) ***The specific heat capacity 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 1K, when its volume is kept constant :

$$c_v = \left(\frac{\Delta Q}{\Delta T}\right)_V \qquad (10.19)$$

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

$$c_p = \left(\frac{\Delta Q}{\Delta T}\right)_P \qquad (10.20)$$

When 1 mole of a gas is considered, we define ***molar heat capacity.***

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 used up in two parts :

(i) heat required to do external work to produce a change in volume of the gas, and

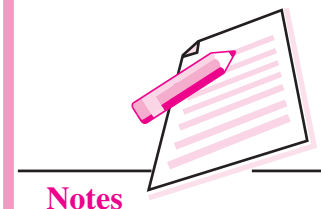
(ii) heat required to raise the temperature of the gas through one degree ($c_v$).

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

$$c_p = W + c_v \qquad (10.21)$$

## 10.7 RELATION BETWEEN $C_P$ AND $C_V$

Let us consider one mole of an ideal gas enclosed in a cylinder fitted with a frictionless movable piston (Fig. 10.5). Since the gas has been assumed to be ideal (perfect), there is no intermolecular force between its molecules. When such a gas expands, some work is done in overcoming internal pressure.





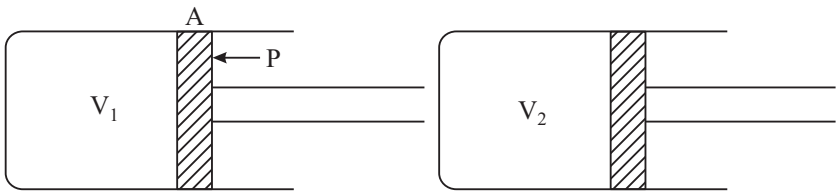



**Fig. 10.5 :** Gas heated at constant pressure

Let P be the external pressure and *A* be the cross sectional area of the piston. The force acting on the piston = P × *A*. Now suppose that the gas is heated at constant pressure by 1K and as a result, the piston moves outward through a distance *x*, as shown in Fig. 10.5. 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 a distance *x*, against external pressure P is given by

$$W = P \times A \times x$$

$$= P \times (\text{Increase in volume})$$

$$= P (V_2 - V_1)$$

We know from Eqn. (10.22) that $c_p - c_v$ = Work done (*W*) against the external pressure in raising the temperature of 1 mol of a gas through 1 K, i.e.

$$c_p - c_v = P (V_2 - V_1) \qquad (10.22)$$

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

$$PV_1 = RT \qquad (10.23)$$

$$PV_2 = R (T + 1) \qquad (10.24)$$

Substracting Eqn. (10.23) from Eqn.(10.24), we get

$$P (V_2 - V_1) = R \qquad (10.25)$$

Hence from Eqns. (10.19) and (10.22) we get

$$c_p - c_v = R \qquad (10.26)$$

where R is in J $mol^{-1}$ $K^{-1}$

Converting joules into calories, we can write

$$c_p - c_v = \frac{R}{J} \qquad (10.27)$$

where J = 4.18 cal is the mechanical equivalent of heat.

**Example 10.5 :** Calculate 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 mol of a gas is given as

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

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 $E_T$ denotes total energy of gas at T K and $E_{T+1}$ signifies total energy of gas at (T + 1) K, then $c_v = E_{T+1} - E_T$ .

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

$$\therefore \quad \text{monoatomic gas } c_V = \frac{3}{2} R (T + 1) - \frac{3}{2} R T = \frac{3}{2} R.$$

Hence $$c_p = c_V + R = \frac{3}{2} R + R = \frac{5}{2} R.$$

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

$$\therefore \quad c_V = \frac{5}{2} R (T + 1) - R \frac{5}{2} R T = \frac{5}{2} R$$

$$c_p = c_V + R = \frac{5}{2} R + R = \frac{7}{2} R.$$

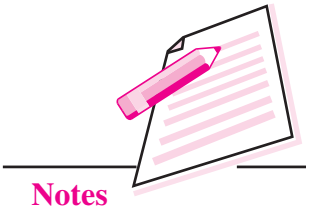
(iii) You should now find out $c_V$ and $c_p$ for triatomic gas.

## INTEXT QUESTIONS 10.3

1. What is the total energy of a nitrogen molecule?
2. Calculate the value of $c_p$ and $c_V$ for nitrogen (given, R = 8.3J $mol^{-1}$ $K^{-1}$).
3. Why do gases have two types of specific heat capacities?

### Brownian Motion and Mean Free Path

Scottish botanist Robert Brown, while observing the pollen grains of a flower suspended in water, under his microscope, found that the pollen grains were tumbling and tossing and moving about in a zigzag random fashion. The random motion of pollen grains, was initially attributed to live objects. But when motion of pollens of dead plants and particles of mica and stone were seen to exhibit





the same behaviour, it became clear that the motion of the particles, now called **Brownian motion,** was caused by unbalanced forces due to impacts of water molecules. Brownian motion provided a direct evidence in favour of kinetic theory of matter. The Brownian displacement was found to depend on.

(i) Size of the particles of the suspension – smaller the particles, more the chances of inbalanced impacts and more pronounced the Brownian motion.

(ii) The Brownian motion also increases with the increase in the temperature and decreases with the viscosity of the medium.

Due to mutual collisions, the molecules of a fluid also move on zig-zag paths. The average distance between two successive collisions of the molecules is called mean free path. The mean free path of a molecule is given by

$$\sigma = \frac{1}{\sqrt{2}\, n \pi d^2}$$

where $n$ is the number density and $d$ the diameter of the molecules.

## WHAT YOU HAVE LEARNT

- The specific heat of a substance is defined as the amount of heat required to raise the temperature of its unit mass through 1°C or 1 K.
- According to principle of calorimetry: Heat lost = Heat gained
- 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 macroscopic properties to microscopic properties of individual molecules.
- The pressure of a gas is the average impact of its molecules on the unit area of the walls of the container.
- Kinetic energy of a molecule depends on the absolute temperature T and is independent of its mass.
- At absolute zero of temperature, the kinetic energy of a gas is zero and molecular motion ceases to exist.
- Gas law can be derived on the basis of kinetic theory. This provided an early evidence in favour of kinetic theory.
- Depending on whether the volume or the pressure is kept constant, the amount of heat required to raise the temperature of unit mass of a gas by 1ºC is different. Hence there are two specific heats of gas :

i) Specific heat capacity at constant volume ($c_V$)

ii) Specific heat capacity at constant pressure ($c_p$)

These are related as $c_p = W + c_V$

$$c_p - c_V = \frac{R}{J}$$

- The degrees of freedom of a system of particles are the number of independent ways in which the particles of the system can move.
- The law of equipartition of the energy states that the total kinetic energy of a dynamical system is distributed equally among all its degrees of freedom and it is equal to $\frac{1}{2}$ k T per degree of freedom.
- Total energy for a molecule of (i) a monatomic gas is $\frac{3}{2}$ k T, (ii) a diatomic gas is $\frac{5}{2}$, and (iii) a triatomic gas is 3 k T.

## TERMINAL EXERCISE

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 is raised four times, what will happen to its kinetic energy, root-mean square velocity and pressure?
4. What should be the ratio of the average velocities of hydrogen molecules (molecular mass = 2) and that of 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 $s^{-1}$ respectively, calculate the ratio between their root mean square and average speeds.
6. Explain what is meant by the root-mean square velocity of the molecules of a gas. Use the concepts of kinetic theory of gases to derives an expression for the root-mean square velocity of the molecules in term of pressure and density of the gas.
7. i) Calculate the average translational kinetic energy of a neon atom at 25 $^0$C.

   ii) At what temperature does the average energy have half this value?

8. A container of volume of 50 $cm^3$ contains hydrogen at a pressure of 1.0 Pa and at a temperature of 27 $^0$C. Calculate (a) the number of molecules of the gas in the container, and (b)their root-mean square speed.

   ( R= 8.3 J $mol^{-1}$ $K^{-1}$ , N = $6 \times 10^{23}$ $mol^{-1}$. Mass of 1 mole of hydrogen molecule = $20 \times 10^{-3}$ kg $mol^{-1}$).

9. A closed container contains hydrogen which exerts pressure of 20.0 mm Hg at a temperature of 50 K.

   (a) At what temperature will it exert pressure of 180 mm Hg?

   (b) If the root-mean square velocity of the hydrogen molecules at 10.0 K is 800 m $s^{-1}$, 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 the pressure of a gas.

12. Deduce Boyle's law and Charle's law from kinetic the theory of gases.

13. What is the interpretation of temperature on the basis of kinetic theory of gases?.

14. What is Avagardo'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 and at 100 $^0$C (Density of hydrogen at 0°C and 760 mm of mercury pressure = 0.09 kg $m^{-3}$).

16. Calculate the pressure in mm of mercury exerted by hydrogen gas if the number of molecules per $m^3$ is $6.8 \times 10^{24}$ and the root-mean square speed of the molecules is $1.90 \times 10$ m $s^{-1}$. Avogadro's number $6.02 \times 10^{23}$ and molecular weight of hydrogen = 2.02).

17. Define specific heat of a gas 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 triatomic gas $c_V = 3R$

19. Calculate $c_p$ and $c_V$ for argon. Given R = 8.3 J $mol^{-1}$ $K^{-1}$.

## ANSWERS TO INTEXT QUESTIONS

### 10.1

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 kinetic theory of molecules is called as an ideal gas.

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

4. The specific heat of a substance is the amount of heat required to raise the temperature of its unit mass through 1°C or 1K.

5. The coefficient of cubical expansion is defined as the change in volume per unit original volume per degree rise in temperature.

6. 0.00005 $°C^{-1}$

## 10.2

1. Average speed $\overline{c}$

$$= \frac{500 + 600 + 700 + 800 + 900}{5}$$

$= 700 \text{ m s}^{-1}$

Average value of $\overline{c}^2$

$$= \frac{500^2 + 600^2 + 700^2 + 800^2 + 900^2}{5}$$

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

$c_{rms} = \sqrt{\overline{c^2}} = \sqrt{510{,}000} = 714 \text{ m s}^{-1}$

$c_{rms}$ and $\overline{c}$ are not same

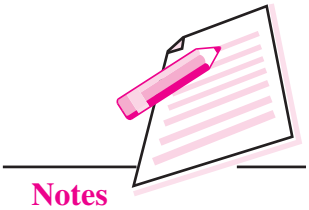
2. The resultant pressure of the mixture will be the sum of the pressure of gases 1 and 2 respectively i.e. $P = P_1 + P_2$.

3. Boyle's law is not applicable.

## 10.3

1. For each degree of freedom, energy = $\frac{1}{2}$k T

$\therefore$ for 5 degrees of freedom for a molecule of nitrogen, total energy = $\frac{5}{2}$k T.





2. $c_V$ for a diatomic molecule = $\frac{5}{2}$ R

$c_V = \frac{5}{2} \times 8.3$ J mol$^{-1}$ K$^{-1}$ = 20.75 J mol$^{-1}$ K$^{-1}$.

$c_p = c_V + R = 29.05$ J mol$^{-1}$ C$^{-1}$.

## Answers to Terminal Problem

2. zero
3. becomes 4 times, doubles, becomes 4 time.
4. 4 : 1
5. 2
7. $6.18 \times 10^{-21}$ m s$^{-1}$, – 124 ºC
8. $12 \times 10^{20}$, $7.9 \times 10^{11}$ m s$^{-1}$
9. 2634ºC, 2560 m s$^{-1}$
15. 1800 m s$^{-1}$, 2088 m s$^{-1}$
16. $3.97 \times 10^{3}$ N m$^{-2}$
17. 12.45 J mol$^{-1}$ K$^{-1}$, 20.75 J mol$^{-1}$ K$^{-1}$.