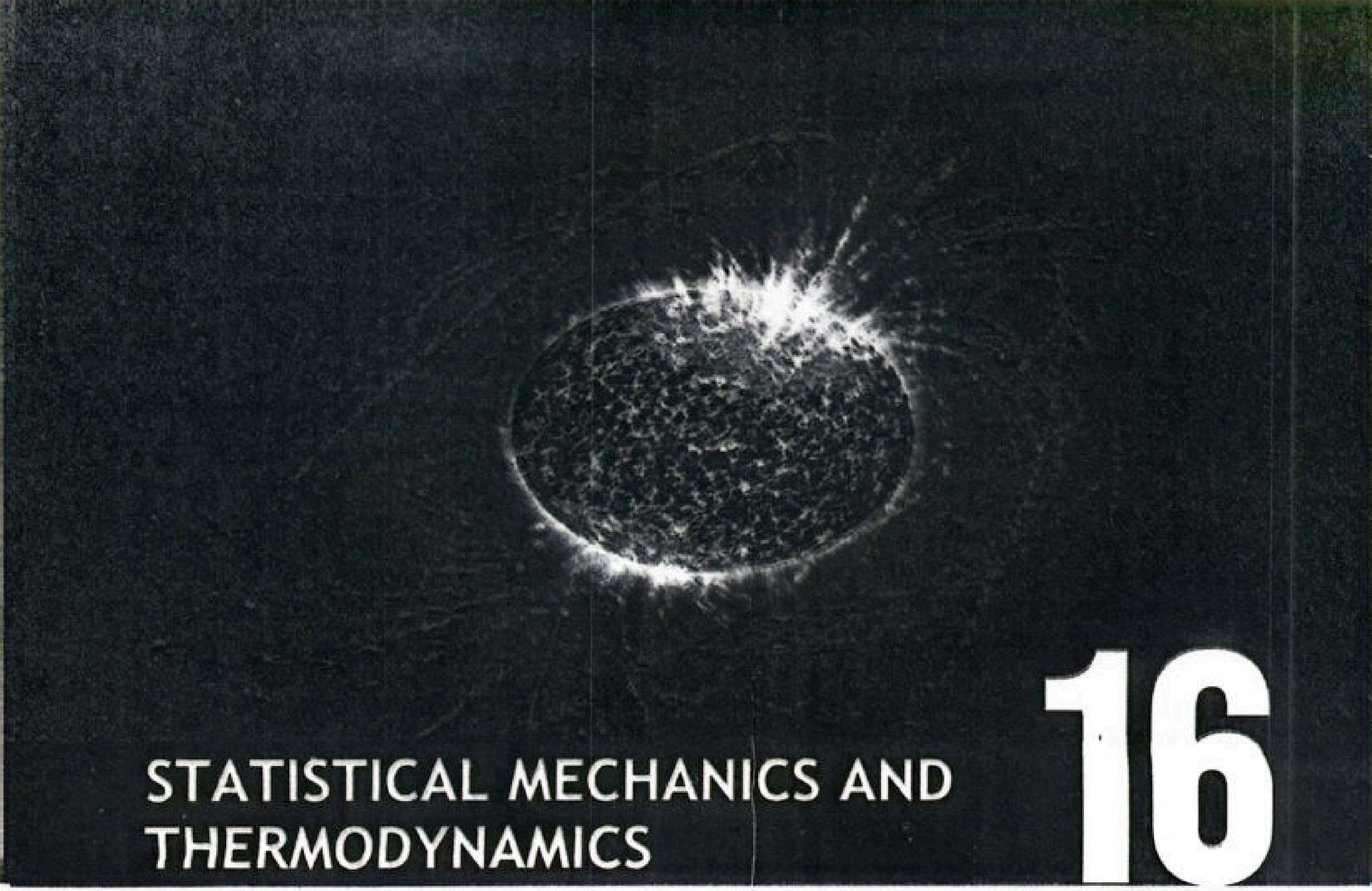


16

STATISTICAL MECHANICS AND THERMODYNAMICS

Student Learning Outcomes (SLOs)

The student will

- explain how molecular movement causes the pressure exerted by a gas.
- Derive and use the relationship $PV=1/3Nm<c^2>$ [where $<c^2>$ is the mean-square speed (a simple model considering one-dimensional collisions and then extending to three dimensions using $1/3<c^2>=<c_x^2>$ is sufficient)].
- Calculate the root-mean-square speed of an ideal gas.
- Derive and use the formula for the average translational kinetic energy of a gas.
- Illustrate that the model of ideal gasses is used a base from which the field of statistical mechanics emerged [and has helped explain the behavior of 'non-ideal' gasses through modifications to the model e.g. the behavior of stars].
- State that under extreme physical conditions, atoms can break down into sub-atomic particles that can form unusual states of matter [Such as degenerate matter. Usually made of any one kind of subatomic particle such as neutron degenerate matter in neutron stars under strong gravity and heat) and Bose-Einstein condensates (created when certain materials are taken to very low temperatures and then exhibit remarkable properties like superconductivity and superfluidity)].

Statistical mechanics provides a foundation for understanding thermodynamic properties like energy, entropy, and temperature by using the principles of thermodynamics.

Statistical mechanics is a branch of physics that applies statistical methods to understand the behavior of physical systems composed of a large number of particles. It offers a framework for understanding the behavior of complex systems, from the microscopic to the macroscopic level. In the present chapter, we shall relate volume, pressure, and temperature to the microscopic properties like speed and kinetic energy of gas molecules. Statistical mechanics is applied to various complex systems, from materials science to biological systems.

16.1 PRESSURE EXERTED BY GAS MOLECULES

The molecules of a gas are in a state of continuous random motion in a container. They collide with one another and also with the walls of the container. Due to collisions of gas molecules with the walls, their momentum changes. Due to their elastic collisions, they transfer an equal amount of momentum to the walls of the container. According to Newton's second law of motion, the rate of transfer of momentum ($\Delta p/\Delta t$) by the gas molecules to the walls is equal to the force (F) exerted on the wall. This force exerted by the gas molecules per unit area (A) of the walls is equal to the pressure exerted by the gas.

$$\text{Pressure} = \frac{F}{A} = \left(\frac{\Delta p}{\Delta t}\right)\frac{1}{A}$$

Hence, the pressure that the gas exerts on the box depends upon the number of molecules that hit each side of the box in one second and the force with which a molecule collides with the wall.

Let us consider an ideal gas consisting of N number of identical molecules in a rapid, random motion contained in a cubic box of side l, as shown in Fig. 16.1. The gas molecules are moving with velocity (v) collide with the walls of the container and exert force on it. The force exerted per unit area of the wall is the pressure of the gas.

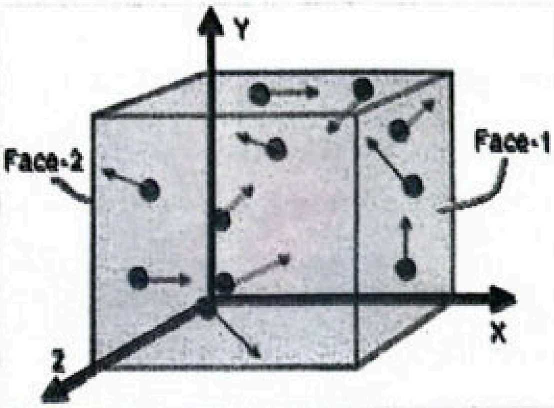


Figure 16.1: Collision of gas molecules with the wall of container.

Consider a single gas molecule of mass "m" moving towards face-1 of the container with the x-component of its velocity v_{x1}. So, initial momentum of the molecule along the x-direction is mv_{x1}. At face-1 of the container, the molecule has perfectly elastic collision and bounces back, (its momentum is reversed). So, after the collision final momentum in the negative x-direction is $-mv_{x1}$. Therefore, change in momentum of a gas molecule along the x-direction is:

$$\Delta p = -mv_{x1} - (mv_{x1})$$

$$\Delta p = -2mv_{x1} \quad \text{\_\_\_\_\_\_} (16.1)$$

According to the law of conservation of momentum, the momentum imparted to the wall by the molecule will be $2mv_{x1}$.

After colliding with face-1 of the container, the molecule travels to opposite face-2 and collide with it, rebounds, and travels back to face-1. So, the gas molecule cover distance '2l' before it again collides with face-1. The time Δt taken by gas molecule to covers this distance '2l' is given by:

$$\Delta t = \frac{2l}{v_{x1}} \quad \_\_\_\_\_\_ \ (16.2)$$

So, the rate of change of momentum of a gas molecule along x-axis is:

$$\frac{\Delta p}{\Delta t} = \frac{-2mv_{x1}}{\frac{2l}{v_{x1}}} = \frac{-mv_{x1}^2}{l} \quad \_\_\_\_\_\_ \ (16.3)$$

As the rate of change of momentum is equal to force. Therefore, force exerted by wall of cubical container on gas molecule is $\frac{-mv_{x1}^2}{l}$. According to Newton's third law of motion, the force exerted by the gas molecule on wall of cubical container is equal in magnitude but opposite in direction to the force exerted by wall on gas molecule. Force F_{x1} exerted by gas molecule on the wall of cubical container is given by

$$F_{x1} = -\left(\frac{-mv_{x1}^2}{l}\right) = \frac{mv_{x1}^2}{l}$$

Similarly, forces exerted by all other molecules along x-axis are:

$$F_{x2} = \frac{mv_{x2}^2}{l},\ F_{x3} = \frac{mv_{x3}^2}{l},\ \dots,\ F_{xN} = \frac{mv_{xN}^2}{l}$$

Total force exerted F_x due to all molecules along x-axis is

$$F_x = F_{x1} + F_{x2} + F_{x3} + \dots + F_{xN}$$

or

$$F_x = \frac{mv_{x1}^2}{l} + \frac{mv_{x2}^2}{l} + \frac{mv_{x3}^2}{l} + \dots + \frac{mv_{xN}^2}{l}$$

$$F_x = \frac{m}{l}(v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2)$$

Multiplying and dividing R.H.S by N number of gas molecules.

$$F_x = \frac{mN}{l}\left(\frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2}{N}\right) \quad \_\_\_\_\_\_ \ (16.4)$$

Where 'mN' is total mass of N gas molecules. Putting $\left(\frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \dots + v_{xN}^2}{N}\right) = \langle v_x^2 \rangle$ in Eq. (16.4), we get:

$$F_x = \frac{mN}{l}\langle v_x^2 \rangle \quad \_\_\_\_\_\_ \ (16.5)$$

Where $\langle v_x^2 \rangle$ is the mean square velocity of all the gas molecules traveling along the x-direction. The mean square velocity $\langle v^2 \rangle$ of the gas molecule is equal to the sum of the mean square velocities of the x, y, and z-components of velocities.

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \quad \_\_\_\_\_\_ \ (16.6)$$

Due to the random motion of a large number of gas molecules in the container, the components of the mean square velocities of the gas molecules are the same along three axes, i.e., $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$. So, Eq. (16.6) becomes as:

$$\langle v^2\rangle = \langle v_x^2\rangle + \langle v_x^2\rangle + \langle v_x^2\rangle \quad \text{or} \quad \langle v^2\rangle = 3\langle v_x^2\rangle$$

or
$$\langle v_x^2\rangle = \frac{\langle v^2\rangle}{3} \qquad \_\_\_\_\_ (16.7)$$

Putting value of $\langle v_x^2\rangle$ from Eq. (16.7) in Eq. (16.5), we get:

$$F_x = \frac{mN}{l}\frac{\langle v^2\rangle}{3}$$

As the force per unit area in unit time on all faces of a cubical container is equal, therefore generalizing the above equation, we get:

$$F = \frac{mN}{l}\frac{\langle v^2\rangle}{3} \qquad \_\_\_\_\_ (16.8)$$

Also, according to Pascal's law, the pressure of gas is equally transmitted on all faces of a cubical container. Since pressure is the force per unit area, therefore,

$$P = \frac{\text{Force}}{\text{Area}} = \frac{F}{l^2} \qquad \_\_\_\_\_ (16.9)$$

Putting value of F from Eq. (16.8) in Eq. (16.9), we get:

$$P = \frac{mN}{l}\frac{\langle v^2\rangle}{3}\left(\frac{1}{l^2}\right)$$

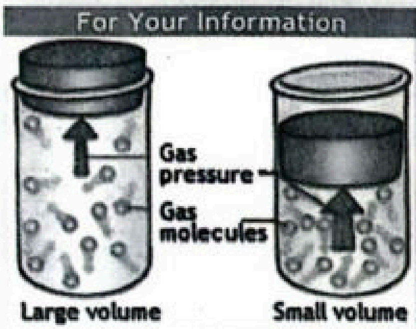
or
$$P = \frac{mN}{l^3}\frac{\langle v^2\rangle}{3}$$

As l^3=V (Volume of the gas), so above equation becomes:

$$P = \frac{mN}{3V}\langle v^2\rangle \qquad \_\_\_\_\_ (16.10)$$

This is the expression for the pressures of ideal gas.

For Your Information



Pressure is affected by volume. As the volume of the container decreases molecules contained within a smaller volume. As a result, the particle collisions occur more frequently with the sides of the container, exerting a higher pressure.

When the volume of the container increases, there is more space, so less frequent collisions with the walls of the container, exerting a lower pressure.

Pressure in terms of Average Translational Kinetic Energy of Gas Molecules

To find the relation between pressure of gas and average translational kinetic energy of gas molecules, we multiply and divide the right-hand side of Eq. (16.10) by 2, i.e.,

$$P = \frac{2}{3}\frac{N}{V}\langle\frac{1}{2}mv^2\rangle \qquad \_\_\_\_\_ (16.11)$$

putting $\frac{N}{V} = N_o$ (number of molecules per unit volume), we get:

$$P = \frac{2}{3}N_o\langle\frac{1}{2}mv^2\rangle$$

As, $\frac{2}{3}N_o$ is constant, so;

$$P = \text{constant } \langle\frac{1}{2}mv^2\rangle \qquad \text{or} \qquad P \propto \langle\frac{1}{2}mv^2\rangle$$

or $P \propto \langle K.E \rangle$

This relation shows that:

The pressure exerted by the gas molecules on the walls of container is directly proportional to the average translational kinetic energy of the gas molecules.

Pressure in terms of Density

From Eq. (16.10) we can derive another formula for the pressure of gas in terms of density and mean square velocity of gas molecules.

$$P = \frac{mN}{3V}\langle v^2\rangle$$

As, $\frac{mN}{V} = \rho$, so;

$$P = \frac{1}{3}\rho\langle v^2\rangle \quad \_\_\_\_\_ \ (16.12)$$

This is another expression for the pressures of gas in terms of density of the gas.

Temperature in terms of Average Translational Kinetic Energy of Gas Molecules

According to ideal gas law:

$$PV = n\,RT \quad \_\_\_\_\_ \ (16.13)$$

Where 'n' is the number of moles of the gas, 'V' is the volume, 'T' is the absolute temperature and '$R = 8.314\ \text{J mol}^{-1}\text{K}^{-1}$' is the universal gas constant. As, the number of moles 'n' can be expressed as:

$$n = \frac{N}{N_A}$$

Where $N_A = 6.022 \times 10^{23}$ (molecules or atoms per mole) is the Avogadro number. So, Eq. (16.13) becomes as:

$$PV = N\left(\frac{R}{N_A}\right)T$$

Here $\frac{R}{N_A} = k$ is Boltzmann constant and its value is $1.38 \times 10^{-23}\,\text{JK}^{-1}$. Hence;

$$PV = NkT \quad \_\_\_\_\_ \ (16.14)$$

As, Eq. (16.11) can be written as:

$$PV = \frac{2N}{3}\langle\frac{1}{2}mv^2\rangle \quad \_\_\_\_\_ \ (16.15)$$

Comparing the Eqs. (16.14) and (16.15), we get:

$$N k T = \frac{2N}{3}\langle\frac{1}{2}mv^2\rangle$$

or $$T = \frac{2}{3k}\langle\frac{1}{2}mv^2\rangle \quad \_\_\_\_\_ (16.16)$$

As $\frac{2}{3k}$ = constant, so Eq. (16.16) can be written as:

$$T = \text{constant}\ \langle\frac{1}{2}mv^2\rangle$$

or $$T \propto \langle\frac{1}{2}mv^2\rangle \qquad \text{or} \qquad T \propto \langle K.E\rangle$$

The absolute temperature of an ideal gas is directly proportional to the average translational kinetic energy of the gas molecules.

Example 16.1: The density of the air is $\rho = 1.296$ kg m^{-3} at temperature 0 °C. The root mean square velocity of air molecules is 484 m s^{-1}. Determine the pressure of air.

Given: Density = $\rho = 1.29$ kg m^{-3} $\quad v_{r.m.s} = 484$ m s^{-1} $\quad T = 0$ °C $= 273$ K

To Find: Pressure = P = ?

Solution: By using, $$P = \frac{1}{3}\rho v_{r.m.s}^2$$

Putting values, we get: $$P = \frac{1}{3}\times 1.296\times(484)^2 = 1.012\times10^5\ \text{Pa}$$

Assignment 16.1

Calculate the average translational kinetic energy of a gas molecule at a temperature 320 K.

16.2 ROOT MEAN SQUARE SPEED OF AN IDEAL GAS

According to the kinetic theory of gases, every molecule moves at a different velocity. If v_1, v_2, v_3, ..., v_N are the speeds of N gas molecules, then the mean square speed $\langle v^2\rangle$ can be determined by adding the square of the speeds of all the molecules and dividing it by the total number of gas molecules.

$$\langle v^2\rangle = \frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_N^2}{N}$$

Taking the square root of both sides, we get:

$$\sqrt{\langle v^2\rangle} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_N^2}{N}}$$

Putting $\sqrt{\langle v^2\rangle} = v_{r.m.s}$ on the left side of above equation, we get root mean square speed

$$v_{r.m.s} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_N^2}{N}} \quad \_\_\_\_\_ (16.17)$$

For Your Information

The value of Boltzmann constant per molecule in different units are:

$k = 1.38\times10^{-16}\ erg\ K^{-1}$

$k = 1.38\times10^{-23}\ J\ K^{-1}$

$k = 3.3\times10^{-24}\ cal\ K^{-1}$

The square root of the mean square speed of the gas molecules is called the root mean square (rms) speed of the molecules.

Average speed: It is defined as the arithmetic mean of the speeds of the molecules of a gas at a given temperature.

$$v_{av} = \frac{v_1 + v_2 + v_3 + \ldots. + v_N}{N} \qquad \_\_\_\_\_\_ \ (16.18)$$

In order to derive another expression for the root mean square speed of gas molecules, let us start from the Eq. (16.10) of the pressure of gas.

$$P = \frac{1}{3}\frac{mN}{V}\langle v^2 \rangle$$

or

$$PV = \frac{mN}{3}\langle v^2 \rangle \qquad \_\_\_\_\_\_ \ (16.19)$$

As we know that: $PV = NkT$ ______ (16.20)

Comparing Eqs. (16.19) and (16.20), we get:

$$\frac{mN}{3}\langle v^2 \rangle = NkT$$

$$\langle v^2 \rangle = \frac{3kT}{m} \qquad \_\_\_\_\_\_ \ (16.21)$$

Taking a square root on both sides, we get:

$$v_{r.m.s} = \sqrt{\frac{3kT}{m}} \qquad \_\_\_\_\_\_ \ (16.22)$$

Here $\sqrt{\langle v^2 \rangle} = v_{r.m.s}$. From Eq. (16.22), we can also write as:

$$v_{r.m.s} \propto \sqrt{T}$$

Thus, the root mean square speed of the given gas molecule is directly proportional to the square root of the absolute temperature of the gas molecules.

Putting $k = \frac{R}{N_A}$ in Eq. (16.22), we get:

$$v_{r.m.s} = \sqrt{\frac{3RT}{mN_A}}$$

Putting $mN_A = M$ (molar mass of the gas), we get:

$$v_{r.m.s} = \sqrt{\frac{3RT}{M}} , \qquad \_\_\_\_\_\_ \ (16.23)$$

At constant temperature; $v_{r.m.s} \propto \frac{1}{\sqrt{M}}$

Thus, at constant temperature, the root mean square speed of the gas molecules is inversely proportional to the square root of the molar mass of the gas. A gas of smaller molar mass has comparatively high speed as compared to a gas of greater molar mass. Therefore, the root mean square speed of hydrogen molecules is four times greater than that of oxygen molecules at the same temperature.

Also, from the Eq. (16.12), the pressure of gas is $P = \frac{1}{3}\rho\langle v^2 \rangle$

or $$\langle v^2 \rangle = \frac{3P}{\rho}$$

Taking a square root on both sides of the above equation:

$$\sqrt{\langle v^2 \rangle} = \sqrt{\frac{3P}{\rho}}$$

Putting $\sqrt{\langle v^2 \rangle} = v_{r.m.s}$ on the left side of the above equation:

$$v_{r.m.s} = \sqrt{\frac{3P}{\rho}} \qquad \text{\_\_\_\_\_\_ (16.24)}$$

From Eqs. (16.22), (16.23) and (16.24) we get:

$$v_{r.m.s} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}} \qquad \text{\_\_\_\_\_\_ (16.25)}$$

Example 16.2:

Calculate the root mean square speed of oxygen molecules in the air at standard temperature and pressure.

Given: At ST.P., we have:

Temperature = T = 0 °C = 273 K Pressure = P = 1.01×10^5 Pa

To Find: Root mean square speed of oxygen molecules = $v_{r.m.s}$ = ?

Solution: To find mass m, of one molecule of oxygen, we use the formula

$$m = \frac{\text{Molecular mass of oxygen}}{\text{Avogadro's number}} \quad \text{or} \quad m = \frac{M}{N_A}$$ (For oxygen = M = 32 g)

Thus, $$m = \frac{32\times10^{-3}\,kg}{6.022\times10^{23}} = 5.31\times10^{-26}\ \text{kg}$$

Now for root mean square speed, we use $v_{r.m.s} = \sqrt{\frac{3kT}{m}}$

Putting values, we get: $$v_{r.m.s} = \sqrt{\frac{3\times1.38\times10^{-23}\times273}{5.31\times10^{-26}}} = 461.4\ \text{ms}^{-1}$$

Example 16.3:

Four molecules of a gas have speeds of 2 km s^{-1}, 4 km s^{-1}, 6 km s^{-1}, and 8 km s^{-1}, respectively. Calculate their average speed and root mean square speed.

Given: v_1 = 2 km s^{-1} v_2 = 4 km s^{-1} v_3 = 6 km s^{-1} v_4 = 8 km s^{-1}

To Find: v_{av} = ? $v_{r.m.s}$ = ?

Solution: For average speed, we use the formula: $v_{av} = \frac{v_1 + v_2 + v_3 + v_4}{N}$

Putting values, we get: $$v_{av} = \frac{2+4+6+8}{4} = 5\ \text{km s}^{-1}$$

For root mean square speed, we use the formula:

$$v_{r.m.s} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + v_4^2}{N}}$$

$$v_{r.m.s} = \sqrt{\frac{(2)^2 + (4)^2 + (6)^2 + (8)^2}{4}} = 5.48\ \text{kms}^{-1}$$

Assignment 16.2

Calculate the root mean square speed of nitrogen gas molecules in air under standard conditions of pressure and temperature.

16.3 MODIFICATION OF THE IDEAL GAS MODEL TO DISCUSS BEHAVIOUR OF NON-IDEAL GASES

Behaviour of Ideal Gases

As we know that in the ideal gas model, the size of gas molecules is negligible, there are no interactions between them, and the collisions between each other and with the walls of the container are perfectly elastic.

Gas that obeys the ideal gas law (PV = n RT) is called an ideal gas. The ideal gas law governs macroscopic properties, e.g., temperature, pressure, volume, quantity of gas, and entropy. Although there is no such thing in nature as a truly ideal gas, gases can approach the ideal state at low pressure and high temperatures. We have seen that the temperature of an ideal gas can be determined as $T = \frac{m}{3k}\langle v^2 \rangle$. This equation implies that temperature (a macroscopic property of a gas) is defined by the motion of an individual particle (a microscopic quantity). Hence, different results for ideal gas provide connections between its microscopic and macroscopic quantities. This gives rise to a branch of physics called **statistical mechanics.**

Statistical mechanics is a branch of physics that connects the microscopic details of a system, such as motion, energy, and the interaction of individual particles, with the macroscopic observables we measure, such as temperature, pressure, volume, and entropy.

Statistical mechanics provides a mathematical foundation for thermodynamics, which is otherwise a phenomenological theory.

Behaviour of Non-Ideal Gases

The ideal gas law works well for large volumes, high temperatures, and low pressure, but it fails to explain the behavior of gases under high pressure, high density, and low temperature (where molecules move slowly and interact with each other). It also fails when strong gravitational forces act like those in stars. To account for these deviations from ideal behavior, modifications were made to the ideal gas law.

Van Der Waals Equation

The ideal gas equation PV = n R T can be used for real gases at high temperatures as well as low pressures at which intermolecular forces are negligibly small. Van der Waals modified this equation so that it can be used for real gases at wide ranges of temperature and pressure. Van der Waals assumed that the gas molecules are hard spheres with definite volume and that two gas molecules somehow interact with each other, especially at low temperatures when molecules move slowly. He made the following corrections:

(i) Volume Correction: The size of gas molecules is not negligible, but it has a finite size, and some part of the volume of gas is occupied by the gas molecules. So, the space available for the motion of molecules of gas will be slightly less than the volume of gas 'V'. Roughly 'b' is the volume of one mole of gas molecules. Hence, effective volume becomes (V – b), as shown in Fig. 16.2.

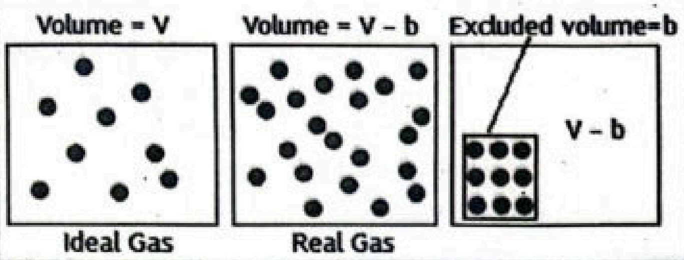


Figure 16.2: Illustration of volume correction.

(ii) Pressure Correction: At low temperature, molecules interact somehow. Inside the container, interaction between gas molecules cancel each other, but particles near the surface and walls of the container have net inward force, as shown in Fig. 16.3. The effective pressure of the real gas is calculated by $\left(P+\frac{a}{V^2}\right)$. Van der Waal's equation for 1 mole of a gas is:

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \_\_\_\_\_\_ \quad (16.26)$$

Here 'a' and 'b' are empirical constants, their values are different for different gases. For 'n' moles of the gas effective volume becomes (V -n b) and effective pressure becomes $\left(P+\frac{an^2}{V^2}\right)$, therefore Vander Waal's equation for 'n' mole of a gas is;

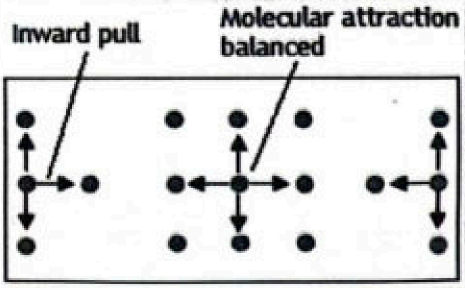


Figure 16.3: Illustration of pressure correction.

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \quad \_\_\_\_\_\_ \quad (16.27)$$

This equation is designed to describe the behavior of real gases, but it can still be used for ideal gases as well. Real gases or non-ideal gases approach ideal behavior at a high temperature and low pressure. At high temperatures or at very low pressure, volume 'V' is very large. So, the terms '$\frac{a}{V^2}$' and 'b' can then be neglected. In this situation, Van der Waals' equation reduces to the ideal gas equation (P V = n RT).

16.4 Gravitational Effects on Ideal Gas Model

In the ideal gas model (i.e., the ideal gas law) at the laboratory scale, gravity is much weaker as compared to other factors such as the kinetic energy of the gas molecules and the pressure of the gas. That's why, it makes sense to ignore gravity for ideal gas. But on a large scale, e.g., in a star, gravity plays an important role in their stability. Accounting for gravity requires much more complex models as compared to the ideal gas model to understand the behaviour of gas molecules.

In the core of stars, heat produced by fusion, radiation pressure, and degeneracy pressure by quantum effects, generate net outward pressure that is counterbalanced by gravity, a state known as hydrostatic equilibrium, as shown in Fig. 16.4. This ensures stability in the stars.

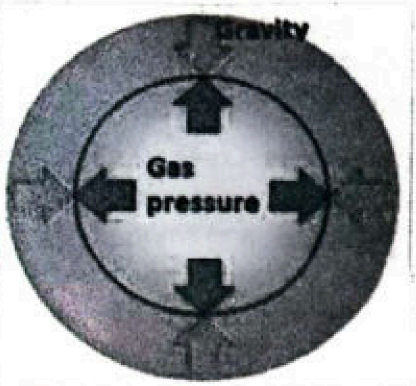


Figure 16.4: Hydrostatic equilibrium.

Example16.4: Calculate the pressure exerted by one mole of a gas at room temperature 300 K with fixed volume 0.022 m^3, using Van der Waals equation. Where a = 3.59 $(\text{liter})^2$ atm $(\text{mole})^{-2}$ and b = 0.0427 liter/mole.

Given: $R = 0.0821$ liter-atm-mol^{-1} K^{-1}

Temperature = T = 300 K n =1 mol

Volume = V = 0.022 m^3 = 0.022×1000 liter = 22 liter

(as 1 m^3 = 1000 liter)

To Find: P = ?

Solution: By using Van der Waals equation: $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$

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

Putting values, we get: $P=\frac{1\times 0.0821\times 300}{22-(1)0.0427}-\frac{3.59\times(1)^2}{(22)^2}=1.1146\text{ atm}$

Assignment 16.3

(a) Using the Van der Waals equation, calculate the temperature of 20.0 moles of helium in a 10.0 *litre* cylinder at 120 atmosphere pressure. Van der Waals constants for helium: a = 0.0341 litre^2 atm mol^{-2}; b = 0.0237 litre mol^{-1}.

(b) Compare this value with the temperature calculated from the ideal gas equation.

16.5 BEHAVIOUR OF MATTER UNDER EXTREME PHYSICAL CONDITIONS

In the universe, there are many cases in which matter has evolved in to extreme physical conditions. Extreme physical conditions can alter the behavior of matter, leading to unique and unusual states of matter such as degenerate matter and phenomena like Bose-Einstein condensation, superconductivity states, superfluidity, and other quantum phenomena. These conditions are observable at extremely high pressure or at extremely low pressure, by materials of high density or by materials experiencing high gravitational force. We will learn how these conditions lead to unusual states of matter.

16.5.1 Degenerate Matter

Extremely high pressure can cause particles to interact closely where quantum mechanical effects, particularly the Pauli Exclusion Principle become significant. The Pauli Exclusion Principle states that:

Two electrons cannot occupy the same quantum state.

Degenerate matter happens when gravity squeezes atoms so tightly under extremely high pressure in a star that they change from their normal state. Normally, atoms are made up of a nucleus and electrons revolving around the nucleus. But when the pressure is extremely high, electrons are strongly pressed tightly against the nucleus in high energy states (according to Pauli Exclusion principle) and they cannot move freely. At this stage, electrons show resistance against gravity and other forces for further compression. This resistance is called degeneracy pressure, which counteract the effect of gravity and other compressive forces, as shown in Fig. 16.5. So, degenerated matter is matter that is packed so tightly that its electrons are forced into a tightly packed configuration.

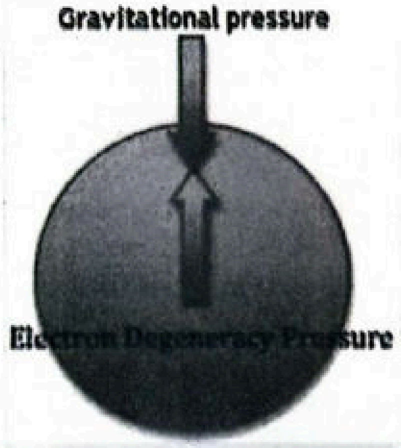


Figure 16.5: Degeneracy pressure.

Degenerate matter is typically formed in the cores of white dwarf and neutron stars, where gravity compress the material to incredibly high densities.

White Dwarfs

White dwarfs are formed due to remnants of low- to intermediate mass- stars. When a star has used up all of its nuclear fusion fuel, it removes its outer layers and contracts to form a white dwarf.

In white dwarfs, the high gravitational force is balanced by electrons degenerate pressure, which arises from the Pauli Exclusion principle, as shown in Fig. 16.6. Gravity pulls material together while electrons are forced into high-energy states, and it forms an equilibrium state.

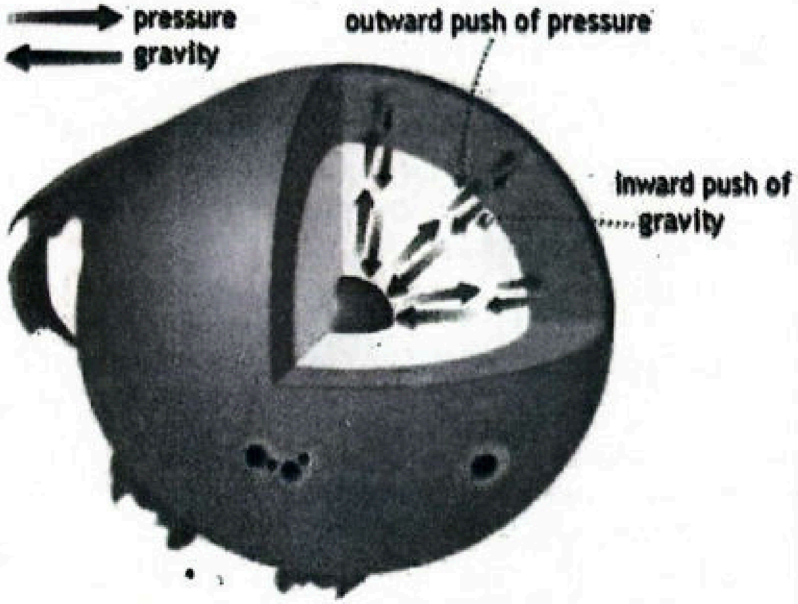


Figure 16.6: High gravitational force is balanced by electrons degenerate pressure.

16.5.2 Neutron Stars

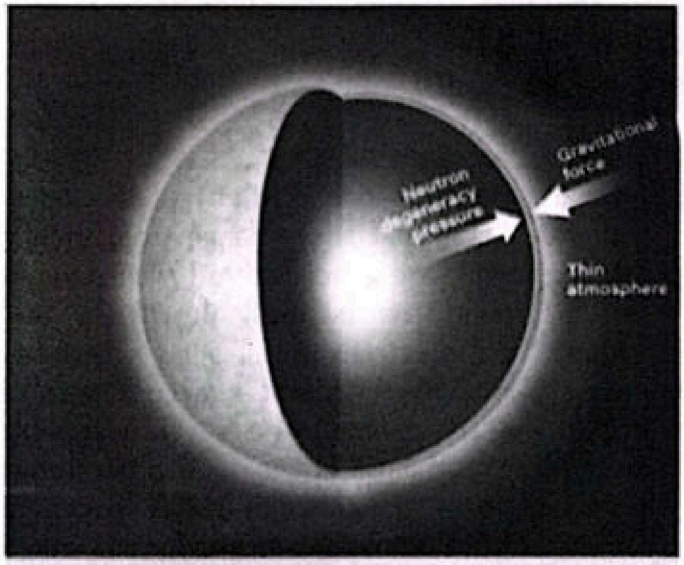


Figure 16.7: Neutron star.

Neutron stars are formed from the remnants of more massive stars. In neutron stars, matter is further compressed by the gravity, due to which electrons and protons start *to combine* to form neutrons. Therefore, neutrons degenerate pressure arises due to the Pauli Exclusion Principle, which balances gravity, preventing further compression, as shown in Fig. ,16.7. This stable state of matter is known as neutron Stars.

Despite the fact, that a neutron star is only about 20 km in diameter, it is about 1.5 times more massive than the sun. Neutron stars have overall densities of the order of 10^{17} kg m^{-3}. Newly formed neutron stars, known as "hot neutron stars," can have a surface temperature of a several million degrees Celsius.

16.5.3 Bose-Einstein Condensation

Bose-Einstein Condensation (BEC) is a state of matter that forms at extremely low temperatures, such as close to absolute zero, causing particles kinetic energies to decrease significantly. At this low temperature, bosons (e.g., photons, W bosons, Z bosons, etc.) can condense in the same state known as Bose-Einstein condensation. This is different from degenerate matter, where two fermions, e.g., electrons, cannot exist in the same state. The Bose-Einstein condensation state of matter exhibits unique properties like superfluidity and superconductivity.

For Your Information

The temperature inside a newly formed neutron star is from around 10^{11} to 10^{12} K. However, the huge number of neutrinos it emits carries away so much energy that the temperature of an isolated neutron star falls within a few years to around 10^6 K.

16.5.4 Super Fluidity

A notable property of Bose-Einstein Condensation is superfluidity, where condensate shows zero viscosity, allowing it to flow without resistance. Superfluidity is observed when certain fluids are cooled to extremely low temperatures, close to absolute zero. This results in special qualities, like a fluid's capacity to pass through incredibly small spaces at a steady speed without the aid of outside forces.

It can also lead to remarkable behaviour, such as the ability to form persistent vortices. In fluid dynamics, a vortex is a region in a fluid in which the flow revolves around an axis line, which may be straight or curved.

16.5.5 Super Conductivity

In certain conditions, Bose-Einstein condensation leads to superconductivity, where electrical resistance drops to zero, allowing current to flow without resistance. This occurs when two electrons form boson-like entities called cooper pairs, which can then occupy the same state and move through the material without scattering.

Below the superconducting transition temperature, paired electrons form a condensate (a macroscopically occupied single quantum state that flows without resistance).

Superconductivity is the property of certain materials to conduct current without energy loss when they are cooled below a critical temperature or transition temperature.

Superconductors are those substances whose resistivity become zero at very low specific temperatures.

Critical temperature (T_c):

The low temperature at which and below which the resistivity ρ of substance become zero is called the critical temperature or superconducting transition temperature, as shown in Fig. 16.8.

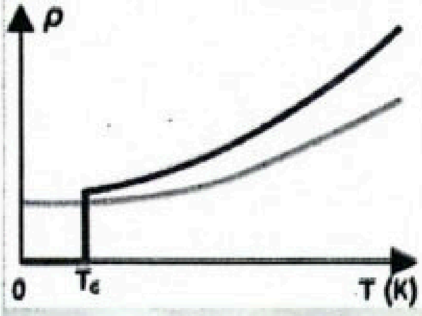


Figure 16.8: Graph of resistivity against temperature.

Superconductivity was first discovered in 1911 by Dutch physicist Heike Kamerlingh Onnes when he observed the sudden disappearance of electrical resistance in mercury at extremely low temperatures (4.2 K). In 1988, some new ceramic (thallium, calcium, barium, coper and oxygen) showed super-conductivity even at critical temperatures of 125 K.

A lanthanum superhydride (LaH_{10}) compound at a pressure of around 170 gigapascals is found to exhibit superconductivity with a critical temperature of 250 kelvin, the highest critical temperature that has been confirmed so far in a superconducting material.

Table: 16.1

Substance	T_c
Mercury (Sb)	4.2 K
Aluminum (Al)	1.18 K
Tin (Sn)	3.72 K
Lead (Pb)	7.2 K

Applications of superconductors:

Superconductors are used in powerful electromagnets (32 Tesla), particle accelerators, magnetic levitation (Maglev) trains, small but powerful electric motors, fast computer chips, and potentially more efficient power transmission lines. Researchers continue to explore ways to achieve superconductivity at higher temperatures, which would make it more practical for everyday use.

SUMMARY

- Pressure of gas: The pressure exerted by a gas molecule is a measure of the force exerted by gas molecules per unit area as they collide with the walls of their container.
- The pressure exerted by the gas molecules on the walls of the container is directly proportional to the average translational kinetic energy of the gas molecules.

- The temperature of gas molecules is directly proportional to the average translational kinetic energy of gas molecules.
- Mean kinetic energy of a moving gas molecule of an ideal gas is directly proportional to the absolute temperature "T".
- Pauli Exclusion Principle states that "two electrons cannot occupy same quantum state".
- Bose-Einstein condensate (BEC) Predicted by Bose and Einstein in the 1920s, this is a unique state of matter at extremely low temperatures, where a group of boson particles occupy the same quantum state.
- Degenerate matter: It's a state of matter where particles are so densely packed that quantum mechanical effects dominate over classical mechanics. This typically occurs in extremely high-pressure environments, such as the cores of massive stars like white dwarfs, neutron stars.
- White dwarfs are formed due to remnants of low to intermediate mass stars. When a star has used up all of its fusion fuel, it removes its outer layers and contracts to form a white dwarf.
- Neutron stars are formed from the remnants of more massive stars. In neutron stars, matter is further compressed by gravity. Due to this, electrons and protons start to combine to form neutrons.
- Super fluidity: A notable property of Bose-Einstein Condensation BEC is superfluidity, where condensate shows zero viscosity, allowing it to flow without resistance.
- Super conductivity: In certain conditions, Bose-Einstein Condensation BEC leads to super-conductivity, where electrical resistance drops to zero, allowing current to flow without resistance.

Formula Sheet

$$P=\frac{mN}{3V}\langle v^2\rangle \qquad P=\frac{2}{3}N_0\langle\frac{1}{2}mv^2\rangle \qquad P=\frac{1}{3}\rho\langle v^2\rangle \qquad T=\frac{2}{3k}\langle\frac{1}{2}mv^2\rangle$$

$$PV = n\,RT \qquad PV = NkT \qquad v_{r.m.s}=\sqrt{\frac{v_1^2+v_2^2+v_3^2+....+v_N^2}{N}}$$

$$v_{r.m.s}=\sqrt{\frac{3kT}{m}}=\sqrt{\frac{3RT}{M}}=\sqrt{\frac{3P}{\rho}} \qquad \left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$$

EXERCISE

Multiple Choice Questions

Encircle the Correct option.

1) Which of the following is the correct relation between pressure 'P' and density 'ρ' of the gas, at constant temperature?

A. $P \propto \frac{1}{\rho}$ B. $P \propto \frac{1}{\rho^2}$ C. $P \propto \rho$ D. $P \propto \rho^2$

2) Which of the following is correct formula for the root mean square speed of a molecule in a gas at the absolute temperature T?

A. $v_{r.m.s} = 1.5\sqrt{\frac{kT}{m}}$ B. $v_{r.m.s} = 1.5\sqrt{\frac{mk}{T}}$ C. $v_{r.m.s} = 1.73\sqrt{\frac{m}{kT}}$ D. $v_{r.m.s} = 1.73\sqrt{\frac{kT}{m}}$

3) Which of the following motions of ideal gas molecules determines the temperature?

A. Translational motion B. Rotational motion
C. Vibrational motion D. All types of motion.

4) Which of the following gases possesses the maximum root mean square velocity at the same temperature?

A. Oxygen B. Carbon dioxide C. Hydrogen D. Helium

5) Real gases deviate from ideal behavior because gas molecules:

A. are colorless B. are spherical
C. have intermolecular forces of attraction D. have high speeds

6) The root mean square speed of gas at 27 °C is $v_{r.m.s}$. If the temperature of the gas is raised to 327 °C , then which of the following will be the root mean square speed of gas?

A. $(1/\sqrt{2})\, v_{r.m.s}$ B. $v_{r.m.s}$ C. $\sqrt{2}\, v_{r.m.s}$ D. $2\, v_{r.m.s}$

7) Which of the following is the ratio of root mean square speed of oxygen O_2 and hydrogen H_2 at same temperature?

A. 1: 2 B. 2:1 C. 1:4 D. 4:1

8) Density of a gas is 5 kg m^{-3} at a pressure of 6×10^5 Pa. Which of the following is the root mean square velocity of the gas molecules?

A. 600 m s^{-1} B. 400 m s^{-1} C. 300 m s^{-1} D. 180 m s^{-1}

9) The average kinetic energy of gas molecules is:

A. directly proportional to pressure of gas B. inversely proportional to volume of gas
C. inversely proportional to the absolute temperature of gas
D. directly proportional to the absolute temperature of gas

10) The pressure is exerted by the gas on the walls of the container because its molecules:

A. lose kinetic energy B. stick to the walls
C. on collision with the walls, there is a change in momentum of gas molecules
D. on collision with the walls, gas molecules exert no force on wall

11) The rms speed of the molecules of enclosed gas is $v_{r.m.s}$. Which of the following will be the rms speed of gas molecule, if pressure is doubled keeping the temperature same?

A. $1/2\, v_{r.m.s}$ B. $v_{r.m.s}$ C. $2\, v_{r.m.s}$ D. $4\, v_{r.m.s}$

12) A neutron star has a super high _______________ .

A. density B. output of light C. input of neutrons D. output of x-rays

13) Which of the following is the electrical resistance of the superconductor below critical temperature?

A. Finite B. Large C. Zero D. Infinity

14) What is the process by which a Bose-Einstein Condensate is formed?

A. Fusion B. Fission
C. Decomposition D. Cooling to extremely low temperature

Short Questions

1) Mention the different ways of increasing the number of molecular collisions per unit time in a gas.
2) By *reducing* the volume of a gas at a constant temperature, the pressure of the gas increases. Explain it on the basis of kinetic theory.
3) What do you mean by the root mean square speed of the molecules of a gas? Is the root mean square speed the same as the average speed?
4) Why is the temperature below absolute zero not possible?
5) Estimate the average kinetic energy of a helium atom at the temperature on the surface of the sun (6000 K).
6) Show that the ratio of the root mean square speeds of molecules of two different gases at a certain temperature is equal to the square root of the inverse ratio of their masses.
7) Differentiate between the formations of white dwarfs and neutron stars.
8) Why do the gases at low temperatures and high pressure show large deviations from ideal behaviour?
9) What distinguishes degenerate matter from regular matter?
10) Show that the temperature of ideal gas is directly proportional to the average translational kinetic energy of gas molecules.
11) What happens to the electrical resistance of a superconductor when it is cooled below its critical temperature?
12) What are some potential applications of superconductors in transportation?
13) Provide an example of a high-temperature superconductor.

Comprehensive Questions

1) What is the pressure of gas? How do gas molecules exert pressure on the walls of a container?
2) Derive an expression for the pressure of an ideal gas and show that pressure is directly proportional to the average translational kinetic energy of gas molecules.
3) Describe the root mean square speed of the ideal gas molecule and drive its expressions.
4) Derive an expression for the average translational kinetic energy of the ideal gas molecule.
5) Describe the modification of the ideal gas model to discuss the behaviour of non-ideal gases using the Wan der Waals equation.
6) Describe the behaviour of matter under extreme physical conditions. What is degenerate matter, and how are white dwarf and neutron stars formed?
7) Discuss superfluidity and superconductivity on the basis of Bose-Einstein condensation.

Numerical Problems

1) The mass of a helium atom is 6.64×10^{-27} kg. Calculate the root mean square speed of helium atom in a gas at a temperature of 15 °C. **(Ans: 1.34×10^{3} m s^{-1})**

2) At which temperature will the root mean square velocity of the oxygen molecules become equal to the escape velocity of the earth (11.2 km s^{-1})? (Mass of one molecule of oxygen is 5.3×10^{-26} kg and Boltzmann constant $k = 1.38\times10^{-23}$ J K^{-1}). **(Ans: 1.6×10^{5} K)**

3) The mass of a molecule of a gas is 6.4×10^{-27} kg. Calculate the root mean square speed of gas molecule and kinetic energy per molecule at temperature 400 K.

(Ans: 1.6×10^{3} m s^{-1}, 8.3×10^{-21} J)

4) At which temperature the root mean square speed of gas molecules becomes double than its speed at 27 °C, (pressure of gas is kept constant)? **(Ans: 927 °C)**

5) Determine the root mean square speed of argon atoms at temperature 40 °C. The molar mass of argon is 39.95 g mol^{-1}. **(Ans: 442 m s^{-1})**

6) Calculate the number of gas molecules in a cubic meter of gas at standard temperature and pressure (STP). **(Ans: 2.68×10^{25} molecules)**

7) A vessel A contains hydrogen and another vessel B whose volume is twice of vessel A contains same mass of oxygen at the same temperature. Find (i) the ratio of the root mean square speeds of hydrogen and oxygen gases, (ii) the ratio of pressures of gases in vessels A and B. Molecular mass of hydrogen and oxygen are 2 and 32 respectively. **(Ans: 4:1 and 32:1)**