3. Kinetic Theory of Gases and Radiation

Can you recall?

1. What are different states of matter?
2. How do you distinguish between solid, liquid and gaseous states?
3. What are gas laws?
4. What is absolute zero temperature?
5. What is Avogadro number? What is a mole?
6. How do you get ideal gas equation from the gas laws?
7. How is ideal gas different from real gases?
8. What is elastic collision of particles?
9. What is Dalton's law of partial pressures?

3.1. Introduction:

You have been introduced to the three common states of matter viz. solid, liquid and gas. You have also studied the gas laws: Boyle's law, Charles' law, and Gay-Lussac's law. The ideal gas equation can be obtained from the three gas laws.

The volume V of a gas is inversely proportional to the pressure P, temperature being held constant. Separately, volume V and pressure P are directly proportional to temperature. In a nut shell,

Boyle's law: $V \propto 1/P$ at constant T --- (3.1)

Charles' law $V \propto T$ at constant P --- (3.2)

Gay-Lussac's law: $P \propto T$ at constant V--- (3.3)

All the three laws apply to fixed mass m of an enclosed gas.

Combining the three laws into a single relation for a fixed mass of gas yields ideal gas equation. Thus,

$$PV \propto \mathrm{T}, \text{ or } \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Expressing the fixed mass of gas in the above three laws in terms of number of moles n of gas, $PV \propto nT$, or $PV = nRT$,

where number of moles

$$n = \frac{\text{mass of the gas }(M)}{\text{molar mass }(M_0)} = \frac{N}{N_A}$$

(Molar mass is the mass of 1 mole of gas)

Here, proportionality constant R is the universal gas constant, having the same value 8.314 J mol^{-1} K^{-1}, for all the gases, N is the number of molecules in the gas and N_A is the Avogadro number and is the number of molecules in one mole of gas.

Alternatively,

$PV = Nk_BT$, --- (3.4)

where k_B is the Boltznann constant. R and k_B are related by the following relation:

$R = N_A\,k_B$ --- (3.5)

The laws of Boyle, Charles, and Gay-Lussac are strictly valid for real gases, only if the pressure of the gas is not too high and the temperature is not close to the liquefaction temperature of the gas.

A gas obeying the equation of state $PV = nRT$ at all pressures, and temperatures is an ideal gas.

Equation of State: For a gas, its state is specified by a number of physical quantities such as pressure P, temperature T, volume V, internal energy E, etc. Hence, the equation relating these quantities is known as the *equation of state*.

3.2 Behaviour of a Gas:

A stone thrown upwards in air reaches a certain height and falls back to the ground. Its motion can be described well with the help of Newton's laws of motion. A gas enclosed in a container is characterized by its pressure, volume and, temperature. This is the macroscopic description of the gas. You know that the particles of the gas (molecules) are in constant motion. Unlike in the case of motion of the stone, it is very difficult to understand the behaviour of a gas in terms of motion of a single particle (molecule). The number of particles in the gas is itself so large (~ 10^{23} particles per m^3) that any attempt to relate the macroscopic parameters P, V, T and E with the motion of individual particles would be futile.

Hence, certain assumptions are made regarding the particles (molecules) of a gas, averages of physical quantities over the large number of particles involved are obtained and these averages are finally related to the macroscopic parameters of the gas. This is the approach of kinetic theory of gases.

3.3 Ideal Gas and Real Gas:

We know that a gas obeying ideal gas equation at all pressures and temperatures is an ideal gas. In an ideal gas intermolecular interactions are absent. Real gases are composed of atoms or molecules which do interact with each other. Hence, no real gas is truly ideal as defined here. If the atoms/molecules of a real gas are so far apart that there is practically no interatomic/intermolecular interaction, the real gas is said to be in the ideal state. This can happen at sufficiently low density of the real gas. At low pressures or high temperatures, the molecules are far apart and therefore molecular interactions are negligible. Under these conditions, behaviour of real gases is close to that of an ideal gas. Of course, the temperature of the real gas must be well above its liquefaction temperature. Ideal gas serves as a model to deduce certain properties of real gases at least when the real gas is in the ideal state. You have studied deviation of real gas from ideal gas behaviour in XIth Std. Chemistry.

Can you tell?

1. Why is the deviation of real gas from ideal gas behavior observed at high pressure and low temperature?
2. What is the effect of size of the molecules of a real gas, as against the ideal gas comprising point particles, on the properties of the gas ?
3. Does an ideal gas exist in reality?

3.4 Mean Free Path:

How do the molecules of an ideal gas move? These molecules are in continuous random motion such as Brownian motion you have studied in XIth Std. Chemistry.

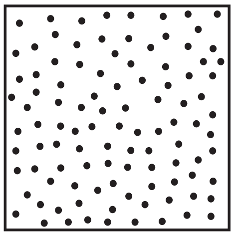


Fig. 3.1 (a): A gas with molecules dispersed in the container: A stop action photograph.

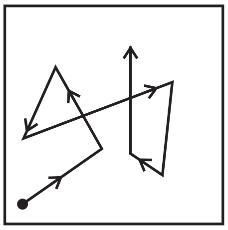


Fig. 3.1 (b): A typical molecule in a gas executing random motion.

The molecules of a gas are uniformly dispersed throughout the volume of the gas as shown in Fig 3.1(a). These molecules are executing random motion. Typical path of a molecule is shown in Fig. 3.1 (b). When a molecule approaches another molecule, there is a repulsive force between them, due to which the molecules behave as small hard spherical particles. This leads to elastic collisions between the molecules. Therefore, both the speed and the direction of motion of the molecules change abruptly. The molecules also collide with the walls of the container. Molecules exert force on each other only during collisions. Thus, in between two successive collisions the molecules move along straight paths with constant velocity. It is convenient and useful to define mean free path (λ), as the average distance traversed by a molecule with constant velocity between two successive collisions. The mean free path is expected to vary inversely with the density of the gas $\rho = \frac{N}{V}$, where N is the number of molecules enclosed in a volume V. Higher the density, more will be the collisions and smaller will be the mean free path λ. It is also seen that λ is inversely proportional to the size of the molecule, say the diameter d. Smaller the size of the molecule, less is the chance for collision and larger is the mean free path. Further, λ is inversely proportional to d^2, not just d, because it depends on the cross section of a molecule. It can be shown that

$$\lambda = \frac{1}{\sqrt{2}\pi\, d^2 (N/V)} \qquad \text{--- (3.6)}$$

Example: 3.1 Obtain the mean free path of nitrogen molecule at 0 °C and 1.0 atm pressure. The molecular diameter of nitrogen is 324 pm (assume that the gas is ideal).

Solution: Given $T = 0\ °C = 273\ K$, $P = 1.0$ atm $= 1.01\times10^5$ Pa and $d = 324$ pm $= 324 \times 10^{-12}$ m.

For ideal gas $PV = Nk_BT$, $\therefore\ \frac{N}{V} = \frac{P}{k_BT}$.

Using Eq. (3.6), mean free path

$$\lambda = \frac{1}{\sqrt{2}\pi d^2\left(\frac{N}{V}\right)} = \frac{k_BT}{\sqrt{2}\pi d^2 P}$$

$$= \frac{\left(1.38\times10^{-23}\,\mathrm{J/K}\right)\left(273\,\mathrm{K}\right)}{\sqrt{2}\pi\left(324\times10^{-12}\,\mathrm{m}\right)^2\left(1.01\times10^5\,\mathrm{Pa}\right)}$$

$$= 0.8\times10^{-7}\,\mathrm{m}$$

Note that this is about 247 times molecular diameter.

If the pressure of a gas in an enclosure is reduced by evacuating it, the density of the gas decreases and the mean free path increases. You must have seen articles coated with metal films. The metals are heated and evaporated in an enclosure. The pressure in the enclosure is reduced so that the mean free path of air molecules is larger than the dimensions of the enclosure. The atoms in the metal vapour then do not collide with the air molecules. They reach the target and get deposited.

3.5 Pressure of Ideal Gas:

We now express pressure of an ideal gas as a kinetic theory problem. Let there be *n* moles of an ideal gas enclosed in a cubical box of volume V ($= L^3$) with sides of the box parallel to the coordinate axes, as shown in Fig. 3.2. The walls of the box are kept at a constant temperature T. The question is: can we relate the pressure P of the gas with the molecular speeds? Here we will use the word molecular speed rather than molecular velocity since the kinetic energy of a molecule depends on the velocity irrespective of its direction.

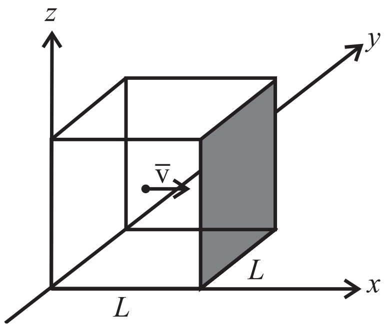
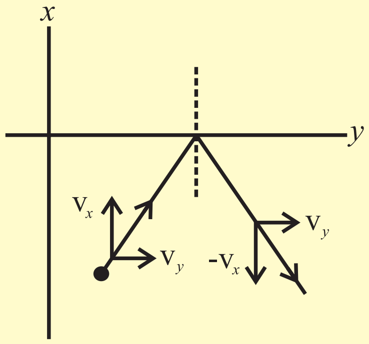


Fig. 3.2: A cubical box of side *L*. It contains *n* moles of an ideal gas. The figure shows a molecule of mass *m* moving towards the shaded wall of the cube with velocity $\vec{v}$.

The gas molecules are continuously moving randomly in various directions, colliding with each other and hitting the walls of the box and bouncing back. As a first approximation, we neglect intermolecular collisions and consider only elastic collisions with the walls. (It is not unphysical to assume this, because, as explained earlier, the mean free path increases as the pressure is reduced. Thus, pressure is so adjusted that the molecules do not collide with each other, but collide with the walls). A typical molecule is shown in the Fig. 3.2 moving with the velocity $\vec{v}$, about to collide with the shaded wall of the cube. The wall is parallel to *yz*-plane. As the collision is assumed to be elastic, during collision, the component v_x of the velocity will get reversed, keeping v_y and v_z components unaltered.

Consider two dimensional elastic collision of a particle with a wall along the *y*-axis as shown in the accompanying figure. It can be easily seen that the v_x component is reversed, v_y remaining unchanged.



Considering all the molecules, their average *y* and *z* components of the velocities are not changed by collisions with the shaded wall. This can be understood from the fact that the gas molecules remain evenly distributed throughout the volume and do not get any additional motion in +*y* or -*y* and +z or -*z* directions. Thus the *y* and *z* components remain unchanged during collision with the wall parallel to the *yz*-plane.

Hence the change in momentum of the particle is only in the *x* component of the momentum, Δp_x is given by

$$\Delta p_x = \text{final momentum - initial momentum}$$
$$= (-mv_x) - (mv_x) = -2\,mv_x \qquad \text{--- (3.7)}$$

Thus, the momentum transferred to the wall during collision is $+\,2mv_x$. The rebounced molecule then goes to the opposite wall and collides with it.

We now set the average force exerted by one molecule on the wall equal to the average rate of change of momentum during the time for one collision. To find this average rate, we have to divide the change in momentum by the time taken for one collision.

After colliding with the shaded wall, the molecule travels to the opposite wall and is reflected back. It travels back towards the shaded wall again to collide with the shaded wall. This means that the molecule travels a distance of 2*L* in between two collisions. Hence to get the average force, we have to divide by the time between two successive collisions.

As *L* is the length of the cubical box, the time for the molecule to travel back and forth to the shaded wall is $\Delta t = \dfrac{2L}{v_x}$.

Average force exerted on the shaded wall by molecule 1 is given as

Average force = Average rate of change of momentum

$$= \frac{2mv_{x1}}{2L/v_{x1}} = \frac{mv_{x1}^2}{L} \qquad \text{--- (3.8)}$$

where v_{x1} is the *x* component of the velocity of molecule 1.

Considering other molecules 2, 3, 4 ... with the respective *x* components of velocities v_{x2}, v_{x3}, v_{x4},..., the total average force on the wall from Eq. (3.8), is

$$= \frac{m}{L}\left(v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \ldots\right)$$

$\therefore$ The average pressure

$$P = \frac{\text{Average force}}{\text{Area of shaded wall}}$$
$$= \frac{m\left(v_{x1}^2 + v_{x2}^2 + \ldots\right)}{L \cdot L^2}$$

The average of the square of the *x* component of the velocities is given by

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + v_{x3}^2 + \ldots v_N^2}{N}$$

$$\therefore P = \frac{mN\overline{v_x^2}}{V} \qquad \text{--- (3.9)}$$

where $\overline{v_x^2}$ is the average over all possible values of v_x.

Now $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$

By symmetry, $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \dfrac{1}{3}\overline{v^2}$ since the molecules have no preferred direction to move. Therefore, average pressure

$$P = \frac{1}{3}\frac{N}{V}m\overline{v^2} \qquad \text{--- (3.10)}$$

Equation (3.10) has been obtained for a cubical shaped container. However, it can be shown to be valid for containers of any shape. Also, we have assumed that there are no inter-molecular collisions. The number of molecules in the container is so large (of the order of 10^{23}) that even if molecular collisions are taken into account, the above expression does not change. If a molecule acquires a velocity with components different than v_x, v_y, v_z after collision, there will invariably be some other molecule having different initial velocity now acquiring the velocity with the components v_x, v_y, v_z. As the gas is steady (in equilibrium), this must be happening. Thus the collisions do not affect Eq. (3.10).

3.6 Root Mean Square (rms) Speed:

Equation (3.10) gives the mean square speed of the molecules of a gas.

$$\overline{v^2} = \frac{3PV}{Nm} \quad \text{--- (3.11)}$$

Using ideal gas equation $PV = nRT$,

$$\therefore \quad \overline{v^2} = \frac{3nRT}{Nm} = \frac{3NRT}{N_A Nm}$$

$$\therefore \sqrt{\overline{v^2}} = v_{rms} = \sqrt{\frac{3RT}{M_0}} \quad , \quad \text{--- (3.12)}$$

where $M_0 = N_A m$ is the molar mass of the gas. Equation (3.12) allows us to estimate rms speeds of molecules of real gases. For nitrogen gas, at 300 K, the rms speed in 517 m/s, while for oxygen gas it is 483 m/s.

You have studied passage of sound waves through air medium. Speed of sound in a gas is $v_s = \sqrt{\frac{\gamma RT}{M_0}}$, where $\gamma = \frac{C_P}{C_V}$ is called the adiabatic ratio. Its maximum value is 5/3, for monatomic gases. The sound wave cannot move faster than the average speed of the molecules (since $\gamma < 3$). However, the two speeds are of the same order of magnitude. The molecules serve as a medium to transport sound energy. The speed of sound in H_2 gas is comparable to the rms speed of H_2 molecules and in N_2 gas to the rms speed of N_2 molecules.

3.7 Interpretation of Temperature in Kinetic Theory:

Equation (3.10) can be written as

$$PV = \frac{1}{3} Nm\overline{v^2}$$

$$= \frac{2}{3} N \cdot \left(\frac{1}{2} m\overline{v^2} \right) \quad \text{--- (3.13)}$$

The quantity $\frac{1}{2} m\,\overline{v^2}$ is the average translational kinetic energy of a molecule. In an ideal gas, the molecules are noninteracting, and hence there is no potential energy term. Thus, the internal energy of an ideal gas is purely kinetic.

The average total energy E, therefore, is

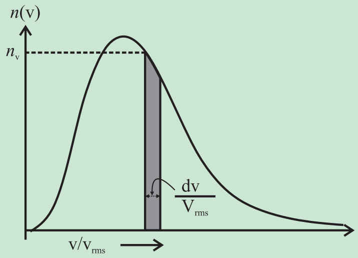
$$E = N \cdot \frac{1}{2} m\overline{v^2} \quad \text{--- (3.14)}$$

From Eq. (3.13),

Do you know?

Distribution of speeds of molecules:

We know that the molecules of a gas are in continuous random motion. Magnitudes of their velocities i.e., the speeds are varying. In the previous sections we saw that root mean square speed, v_{rms}, is a kind of average speed at a given temperature. How many molecules will have speeds greater or smaller than v_{rms}? Molecules can have varying speeds in the range zero to infinity. What is the number of molecules having a particular speed in this range? This function, the number of molecules as a function of the speed is known as the distribution of speeds. Figure shows a typical distribution of speeds for a gas at a temperature T. This is known as Maxwell's distribution of molecular speeds. Here, the shaded area n_v dv is the number of molecules having speed between v and v + dv. Average values of physical quantities like $\overline{v^2}$ can be calculated once the distribution is known.



$$PV = \frac{2}{3} E \quad \text{--- (3.15)}$$

Using ideal gas equation,

$$PV = Nk_B T = \frac{2}{3} E \quad \text{--- (3.16)}$$

$$\therefore E = \frac{3}{2} Nk_B T \quad \text{--- (3.17)}$$

or $$\frac{E}{N} = \frac{3}{2} k_B T \quad \text{--- (3.18)}$$

This means that the average energy per molecule is proportional to the absolute temperature T of the gas. This equation relates the macroscopic parameter of the gas, T, to the kinetic energy of a molecule.

Example 3.2: At 300 K, what is the rms speed of Helium atom? [mass of He atom is 4u, 1u = 1.66×10^{-27} kg; $k_B = 1.38 \times 10^{-23}$ J/K]

Solution: Given $T = 300$ K,

$$m = 4 \times 1.66 \times 10^{-27}\ \text{kg}$$

$$\text{Average } K.E. = \frac{1}{2} m\overline{\text{v}^2} = \frac{3}{2} k_B T$$

$$\therefore \overline{\text{v}^2} = \frac{3k_BT}{m} = \frac{3 \times 1.38 \times 10^{-23} \times 300}{4 \times 1.66 \times 10^{-27}}$$

$$= 187.05 \times 10^4$$

$$\text{v}_{\text{rms}} = \sqrt{\overline{\text{v}^2}} = 13.68 \times 10^2$$

$$= 1368\ \text{m/s}$$

3.8 Law of Equipartition of Energy:

We have seen that the kinetic energy of a single molecule is

$$K.E. = \frac{1}{2} m\text{v}_x^2 + \frac{1}{2} m\text{v}_y^2 + \frac{1}{2} m\text{v}_z^2$$

For a gas at a temperature T, the average kinetic energy per molecule denoted as $\langle K.E. \rangle$ is

$$\langle K.E. \rangle = \left\langle \frac{1}{2} m\text{v}_x^2 \right\rangle + \left\langle \frac{1}{2} m\text{v}_y^2 \right\rangle + \left\langle \frac{1}{2} m\text{v}_z^2 \right\rangle$$

But we know that the mean energy per molecule is $\frac{3}{2}\ k_BT$. Since there is no preferred direction x or y or z,

$$\left\langle \frac{1}{2} m\text{v}_x^2 \right\rangle = \left\langle \frac{1}{2} m\text{v}_y^2 \right\rangle = \left\langle \frac{1}{2} m\text{v}_z^2 \right\rangle = \frac{1}{2} k_B T \quad \text{--- (3.19)}$$

Thus the mean energy associated with every component of translational kinetic energy which is quadratic in the velocity components in *x*, *y* and *z* directions is $\frac{1}{2} k_B T$ and therefore the total translational energy contribution of the molecule is $(3/2)k_BT$.

3.8.1 Degrees of Freedom:

In the above discussion, the molecule as a whole is free to move from one point to the other in the three dimensional space. If it is restricted to move in a plane surface which is two dimensional, then only two coordinates say *x* and *y* will be sufficient to describe its location and two components v_x, v_y will describe its motion in the plane. If a molecule moves along a straight line, then only *x* coordinate and only one velocity component v_x will be sufficient to describe its location and motion along a straight line.

We say that the molecule is free to execute 3, 2, and 1 dimensional translational motion in the above examples. In other words, the molecule in these examples has 3, 2, and 1 degrees/degree of freedom.

Degrees of freedom of a system are defined as the total number of coordinates or independent quantities required to describe the position and configuration of the system completely.

3.8.2 Diatomic Molecules:

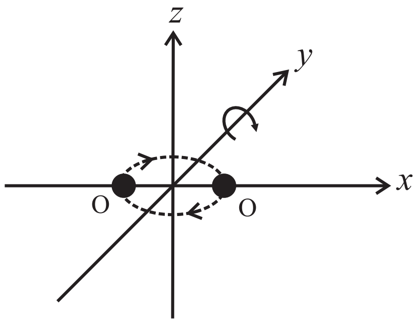


Fig. 3.3: The two independent axes *z* and *y* of rotation of a diatomic molecule such as O_2 lying along the *x*-axis.

Monatomic gas like helium contains He atoms. An He atom has 3 translational degrees of freedom (dof). Consider for example, O_2 or N_2 molecule with the two atoms lying along the *x*-axis. The molecule has 3 translational dof. In addition, it can rotate around *z*-axis and *y*-axis. Figure 3.3 depicts rotation of molecule about the *z*-axis. Like wise, rotation is possible about the *y*-axis. (Note that rotation around the *x*-axis is not a rotation in the sense that it does not involve change of positions of the two atoms of the molecule). In general, a diatomic molecule can rotate about its centre of mass in two directions that are perpendicular to its molecular axis. The molecules like O_2, are therefore, said to possess 2 additional dof namely 2 rotational dof. Each of these 2 dof contribute to rotational kinetic energy. It can be shown that if I_z and I_y are moments of inertia about z and y axes with ω_z and ω_y, the respective angular speeds, the rotational kinetic energies will be $\frac{1}{2}I_z\omega_z^2$ and $\frac{1}{2}I_y\omega_y^2$ for rotation around the two axes. Thus for a diatomic molecule, the total energy due to translational and rotational dof is

$$E = E\,(\text{translational}) + E\,(\text{rotational})$$

$$= \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_z\omega_z^2 + \frac{1}{2}I_y\omega_y^2 \qquad \text{--- (3.20)}$$

The above expression contains quadratic terms that correspond to various dof of a diatomic molecule. Each of them contributes $\frac{1}{2}k_BT$ to the total energy of the molecule. In the above discussion, an implicit assumption was made that the rotating molecule is a rigid rotator. However, real molecules contain covalent bonds between the atoms and therefore can perform additional motion namely vibrations of atoms about their mean positions like a one-dimensional harmonic oscillator. Such molecules therefore possess additional dof corresponding to the different modes of vibration. In diatomic molecules like O_2, N_2 and CO, the atoms can oscillate along the internuclear axis only. This motion adds energy associated with the vibrations to the total energy of the molecule.

$$E = E\,(\text{translational}) + E\,(\text{rotational}) + E\,(\text{vibrational}) \qquad \text{--- (3.21)}$$

The term E (vibrational) consists of two contributions - one from the kinetic energy term and the other from the potential energy term.

$$E\,(\text{vibrational}) = \frac{1}{2}mu^2 + \frac{1}{2}kr^2 \qquad \text{--- (3.22)}$$

where $\vec{u}$ is the velocity of vibrations of the atoms of the molecule, r is the separation between the atoms performing oscillations and k is related to the force constant. The terms in Eq. (3.22) are quadratic in velocity and position respectively and each will contribute $\frac{1}{2}k_BT$. Thus each mode or dof for vibrational motion contributes $2 \times \frac{1}{2}k_BT$ to the total internal energy.

Hence for a non-rigid diatomic gas in thermal equilibrium at a temperature T, the mean kinetic energy associated with the translational motion of molecule along the three directions is $3 \times \frac{1}{2}k_BT$, the mean kinetic energy associated with the rotational motions about two perpendicular axes is $2 \times \frac{1}{2}k_BT$ and total vibrational energy is $2 \times \frac{1}{2}k_BT$ corresponding to kinetic and potential energy terms. Considering the above facts law of equipartition of energy is stated as: **for a gas in thermal equilibrium at a temperature T, the average energy for molecule associated with each quadratic term is** $\frac{1}{2}k_BT$. The law of equipartition of energy is valid for high temperatures and not for extremely low temperatures where quantum effects become important.

3.9 Specific Heat Capacity:

You know that when the temperature of a gas is increased, even a small rise causes considerable change in volume and pressure. Therefore two specific heats are defined for gases, namely specific heat at constant volume C_V and specific heat at constant pressure C_P. Mayer's relation gives an expression that connects the two specific heats.

3.9.1 Mayer's Relation:

Consider one mole of an ideal gas that is enclosed in a cylinder by light, frictionless airtight piston. Let P, V and T be the pressure, volume and temperature respectively of the gas. If the gas is heated so that its temperature rises by dT, but the volume remains constant, then the amount of heat supplied to the gas, dQ_1, is used to increase the internal energy of the gas (dE). Since, volume of the gas is constant, no work is done in moving the piston.

$$\therefore\ dQ_1 = dE = C_V\,dT \qquad \text{--- (3.23)}$$

where C_V is the molar specific heat of the gas at constant volume.

On the other hand, if the gas is heated to the same temperature, at constant pressure, volume of the gas increases by an amount say dV. The amount of heat supplied to the gas is used to increase the internal energy of the gas as well as to move the piston backwards to allow expansion of gas (the work done to move the piston $dW = PdV$)

$$dQ_2 = dE + dW = C_P\,dT \qquad \text{--- (3.24)}$$

where C_P is the molar specific heat of the gas at constant pressure.

But $dE = C_V\,dT$ from Eq. (3.23) as the internal energy of an ideal gas depends only on its temperature.

$$\therefore\ C_P\,dT = C_V\,dT + dW$$

or, $(C_P - C_V)\,dT = P\,dV$ --- (3.25)

For one mole of gas,

$$PV = RT$$

$\therefore\ P\,dV = R\,dT$, since pressure is constant.

Substituting in Eq. (3.25), we get

$$(C_P - C_V)\,dT = R\,dT$$

$$\therefore\ C_P - C_V = R \qquad \text{--- (3.26)}$$

This is known as Mayer's relation between C_P and C_V.

The above relation has been derived assuming that the heat energy and mechanical work are measured in the same units. Generally, heat supplied is measured in calories and work done is measured in joules. The above relation then is modified to $C_P - C_V = R/J$ where J is mechanical equivalent of heat.

Also $C_P = M_0S_P$ and $C_V = M_0S_V$, where M_0 is the molar mass of the gas and S_P and S_V are respective principal specific heats. (In many books, c_P and c_V are used to denote the principal specific heats). Thus,

$$M_0S_P - M_0S_V = R/J$$

$$\therefore S_P - S_V = \frac{R}{M_0 J} \qquad \text{--- (3.27)}$$

Example 3.3: Given the values of the two principal specific heats, S_P = 3400 cal kg^{-1} K^{-1} and S_V = 2400 cal kg^{-1} K^{-1} for the hydrogen gas, find the value of J if the universal gas constant R = 8300 J kg^{-1} K^{-1}.

Solution: Given

S_P = 3400 cal kg^{-1} K^{-1},

S_V = 2400 cal kg^{-1} K^{-1}, R = 8300 J kg^{-1} K^{-1}.

$S_P - S_V = \frac{R}{M_0 J}$ from Eq. (3.27)

$3400 - 2400 = \frac{8300}{2J}$ as $M_0 = 2$ for H_2 gas

Hence, $J = \frac{8300}{2\times1000} = 4.15\ \mathrm{J/cal}\cdot$

Example 3.4: The difference between the two molar specific heats of a gas is 8000 J kg^{-1} K^{-1}. If the ratio of the two specific heats is 1.65, calculate the two molar specific heats.

Solution: Given

$C_P - C_V$ = 8000 J kg^{-1} K^{-1}and $\frac{C_P}{C_V} = 1.65$

since $C_P > C_V$.

$\therefore C_P = 1.65\,C_V$ and $1.65C_V - C_V = 8000$

Solving these, we get

$C_V = \frac{8000}{0.65} = 1.231 \times 10^4$ J kg^{-1} K^{-1} and

$C_P = 8000 + C_V = 2.031 \times 10^4$ J kg^{-1} K^{-1}

It is interesting to use the law of equipartition of energy and calculate the specific heat of gases.

(a) Monatomic Gases: For a monatomic gas enclosed in a container, held at a constant temperature T and containing N_A atoms, each atom has only 3 translational dof. Therefore, average energy per atom is $\frac{3}{2}k_BT$ and the total internal energy per mole is

$$E = \frac{3}{2}N_A k_B T$$

$\therefore$Molar specific heat at constant volume

$$C_V = \frac{dE}{dT} = \frac{3}{2}N_A k_B = \frac{3}{2}R \qquad \text{--- (3.28)}$$

Using Eq. (3.26), $C_P = \frac{5}{2}$ R --- (3.29)

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{5}{3} \qquad \text{--- (3.30)}$$

(b) Diatomic Gases: For a gas consisting of diatomic molecules such as O_2, N_2, CO, HCl, enclosed in a container held at a constant temperature *T*, if treated as a rigid rotator, each molecule will have three translational and two rotational dof. According to the law of equipartition of energy, the internal energy of one mole of gas is

$$E = \frac{3}{2}N_A k_B T + \frac{2}{2}N_A k_B T = \frac{5}{2}N_A k_B T$$

The molar specific heat at constant volume will be

$$C_V = \frac{5}{2}N_A k_B = \frac{5}{2}R \qquad \text{--- (3.31)}$$

Using Eq. (3.26), $C_P = \frac{7}{2}$ R --- (3.32)

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{7}{5} \qquad \text{--- (3.33)}$$

For diatomic gas containing non rigid vibrating molecules, internal energy per mole, considering vibrational motion contributes $k_B T$ per molecule, is

$$E = \frac{3}{2}N_A k_B T + \frac{2}{2}N_A k_B T + \frac{2}{2}N_A k_B T$$

$$= \frac{7}{2}N_A k_B T$$

The molar specific heat at constant volume will be $C_v = \frac{7}{2}N_A k_B = \frac{7}{2}R$ --- (3.34)

Using Eq. (3.26), $C_p = \frac{9}{2}$ R --- (3.35)

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{9}{7} \qquad \text{--- (3.36)}$$

(c) Polyatomic Gases : Gases which have molecules containing more than two atoms are termed as polyatomic gases, e.g., ammonia gas where each molecule has one N atom and three H atoms. Each molecule of the polyatomic gas has three translational dof, each contributing 1/2 $k_B T$ per molecule. Only linear molecules have two dof for rotation. All other polyatomic molecules can perform rotations about three mutually perpendicular axes through their center of mass, hence they have three dof for rotation also. Each rotational dof contributes 1/2 $k_B T$ per molecule. Polyatomic molecules have more than 1 dof for different modes of vibrational motion. The number of dof, *f*, for the vibrational motion of a polyatomic molecule depends on the geometric structure of the molecule i.e., the arrangement of atoms in a molecule. Each such dof contributes average energy 2 × $\frac{1}{2}k_B T$ from kinetic energy and potential energy terms. Therefore for 1 mole of a polyatomic gas, the internal energy is

$$E = \frac{3}{2}N_A k_B T + \frac{3}{2}N_A k_B T + f \times \frac{2}{2}N_A k_B T$$

$$= (3 + f)N_A k_B T$$

and the molar specific heats at constant volume and constant pressure are given as

$$C_V = (3 + f)\,R \qquad \text{--- (3.37)}$$

and $$C_P = (4 + f)\,R \qquad \text{--- (3.38)}$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{4+f}{3+f} \qquad \text{--- (3.39)}$$

Can you recall?

1. What are the different modes of transfer of heat?
2. What are electromagnetic waves?
3. Does heat transfer by radiation need a material medium?

Do you know?

If a hot body and a cold body are kept in vacuum, separated from each other, can they exchange heat? If yes, which mode of transfer of heat causes change in their temperatures? If not, give reasons.

3.10 Absorption, Reflection and Transmission of Heat Radiation:

In XIth Std. you have studied that heat can be transferred by conduction, convection and radiation. The first two modes of heat transfer require a material medium for transmission of heat but radiation does not need a material medium. The most common example of heat transfer by the radiation mode that we come across every day is the transfer of heat and light from the Sun to the earth and to us. In this section, we shall discuss radiation in detail. As the term 'radiation' refers to one mode of transfer of heat, the term 'radiation' also refers to continuous emission of energy from the surface of any body because of its thermal energy. This emitted energy is termed as radiant energy and is in the form of electromagnetic waves. Radiation is therefore the fastest mode of transfer of heat. The process of transfer of heat by radiation does not require any material medium since electromagnetic waves travel through vacuum. Heat transfer by radiation is therefore possible through vacuum as well as through a material medium transparent to this radiation. Physical contact of the bodies that are exchanging heat is also not required. When the radiation falls on a body that is not transparent to it, e.g., on the floor or on our hands, it is absorbed and the body gets heated up. The electromagnetic radiation emitted by the bodies, which are at higher temperature with respect to the surroundings, is known as thermal radiation.

3.10.1 Interaction of Thermal Radiation and Matter:

Whenever thermal radiation falls on the surface of an object, some part of heat energy is reflected, some part is absorbed and the remaining part is transmitted.

Let Q be the total amount of thermal energy incident on the surface of an object and Q_a, Q_r and Q_t be the respective amounts of heat absorbed, reflected and transmitted by the object:

$$\therefore Q = Q_a + Q_r + Q_t\,;$$

dividing by Q, $1 = \frac{Q_a}{Q} + \frac{Q_r}{Q} + \frac{Q_t}{Q}$

$$\therefore\ a + r + t_r = 1 \qquad \text{--- (3.40)}$$

where $a\left(=\frac{Q_a}{Q}\right)$, $r\left(=\frac{Q_r}{Q}\right)$ and $t_r\left(=\frac{Q_t}{Q}\right)$ are the coefficients of absorption, reflection and transmission, respectively.

Coefficient of absorption or absorptive power or absorptivity (*a*): The ratio of amount of heat absorbed to total quantity of heat incident is called the coefficient of absorption.

Coefficient of reflection or reflectance (*r*): The ratio of amount of radiant energy reflected to the total energy incident is called the coefficient of reflection.

Coefficient of transmission or transmittance (t_r): The ratio of amount of radiant energy transmitted to total energy incident is called the coefficient of transmission.

Since all the three quantities a, r and t_r are ratios of thermal energies, they are dimensionless quantities.

If $r = 0$ and $a = 0$, then $t_r = 1$, all the incident energy is transmitted through the object i.e., it is a perfect transmitter. The object is said to be completely transparent to the radiation.

A substance through which heat radiations can pass is known as a *diathermanous substance*. For a diathermanous body, $t_r \neq 0$. A diathermanous body is neither a good absorber nor a good reflector.

Examples of diathermanous substances are glass, quartz, sodium chloride, hydrogen, oxygen, dry air etc.

On the other hand, if $t_r = 0$ and $a + r = 1$, i.e., the object does not transmit any radiation, it is said to be opaque to the radiation.

Substances which are largely opaque to thermal radiations i.e., do not transmit heat radiations incident on them, are known as *athermanous substances*.

Examples of athermanous substances are water, wood, iron, copper, moist air, benzene etc.

If $t_r = 0$ and $a = 0$, then $r = 1$, all the incident energy is reflected by the object i.e., it is a perfect reflector. A good reflector is a poor absorber and a poor transmitter.

If $r = 0$ and $t_r = 0$ then $a = 1$, all the incident energy is absorbed by the object. Such an object is called a perfect blackbody. (We will discuss this in detail later in this chapter)

The values of a, r and t_r also depend on the wavelength of the incident radiation, in addition to the material of the object on which it is incident. Hence, it is possible that an object may be athermanous or diathermanous for certain wavelengths, but is a good absorber for certain other wavelengths.

3.11 Perfect Blackbody:

A body, which absorbs the entire radiant energy incident on it, is called an ideal or perfect blackbody. Thus, for a perfect blackbody, $a = 1$. Any surface that absorbs all the energy incident on it, and does not reflect any energy, therefore, appears black (unless its temperature is very high to be self-luminous). Lamp black or platinum black that absorb nearly 97% of incident radiant heat, resemble a perfect blackbody.

Do you know?

- Can a perfect blackbody be realized in practice?
- Are good absorbers also good emitters?

Consider two objects, which are opaque to thermal radiation, having the same temperature and same surface area. The surface of one object is well-polished and the surface of the other object is painted black. The well-polished object reflects most of the energy falling on it and absorbs little. On the other hand, the black painted object absorbs most of the radiation falling on it and reflects little. But the rate of emission of thermal radiation must be equal to rate of absorption for both the objects, so that temperature is maintained. Black painted object absorbs more, hence it must radiate more to maintain the temperature. Therefore, good absorbers are always good emitters and poor absorbers are poor emitters. Since each object must either absorb or reflect the radiation incident on it, a poor absorber should be a good reflector and vice versa. Hence, a good reflector is also a poor emitter. This is the reason for silvering the walls of vacuum bottles or thermos flasks.

For the study of radiation, a simple arrangement illustrated in Fig. 3.4, which was designed by Ferry, can be used as a perfect blackbody.

3.11.1 Ferry's Blackbody:

It consists of a double walled hollow sphere having tiny hole or aperture, through which radiant heat can enter (Fig. 3.4). The space between the walls is evacuated and outer surface of the sphere is silvered. The inner surface of sphere is coated with lamp-black. There is a conical projection on the inner surface of sphere opposite the aperture. The projection ensures that a ray travelling along the axis of the aperture is not incident normally on the surface and is therefore not reflected back along the same path. Radiation entering through the small hole has negligible chance of escaping back through the small hole. A heat ray entering the sphere through the aperture suffers multiple reflections and is almost completely absorbed inside. Thus, the aperture behaves like a perfect blackbody. In a similar construction, Wien used a cylindrical body with a vertical slit as the aperture. This gives greater effective area as a perfect blackbody.

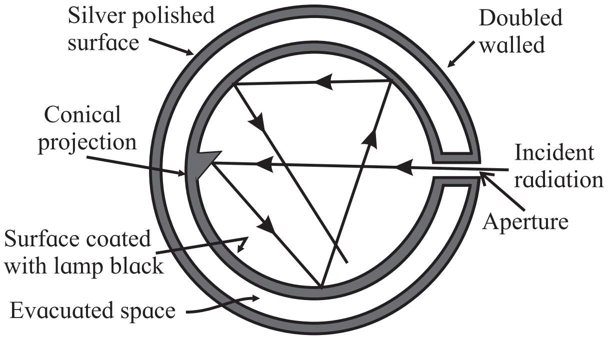


Fig. 3.4: Ferry's blackbody.

Similar working can be achieved using a cavity radiator that consists of a block of material with internal cavity. The inner and outer surfaces are connected by a small hole. The radiation falling on the block that enters through the hole, cannot escape back from it. Hence, the cavity acts as a blackbody. When the block is heated to high temperature, thermal radiation is emitted. This is called cavity radiation and resembles the radiation emitted by a blackbody. Its nature depends only on the temperature of the cavity walls and not on the shape and size of the cavity or the material of the cavity walls. In the kinetic theory of gases, we discussed the theory, properties and various phenomena of an ideal gas rather than dealing with real gases, similarly it is convenient to work with an ideal blackbody.

3.12 Emission of Heat Radiation :

In 1792, Pierre Prevost published a theory of radiation known as theory of exchange of heat. According to this theory, all bodies at all temperatures above 0 K (absolute zero temperature) radiate thermal energy and at the same time, they absorb radiation received from the surroundings. The amount of thermal radiation emitted per unit time depends on the nature of emitting surface, its area and its temperature. Hotter bodies radiate at higher rate than the cooler bodies. Light coloured bodies reflect most of the visible radiation whereas dark coloured bodies absorb most of the incident visible radiation.

For a body, the absorbed radiation (being energy) increases the kinetic energy of the constituent atoms oscillating about their mean positions. You have learnt earlier that the average translational kinetic energy determines the temperature of the body, the absorbed radiation therefore causes a rise in the temperature of the body. The body itself also radiates, therefore its energy decreases, causing lowering of temperature. If a body radiates more than it absorbs, its temperature decreases and vice versa. When the rate of absorption of radiation is same as the rate of emission of radiation, the temperature of the body remains constant and the body is said to be in thermal equilibrium with its surroundings. You might recall the example from XIth Std. of a cup of hot tea ($T_{tea} > T_{room}$) or a plate containing ice ($T_{ice} < T_{room}$) kept on a table, both attain the room temperature after some time. At room temperature also, all bodies radiate as well as absorb radiation, but their rate of emission and rate of absorption are same, hence their temperature remains constant. You can therefore infer that hot bodies would radiate more than cooler bodies.

At room temperature (in fact for temperatures T lower than 800 °C), the thermal radiation corresponds to wavelengths longer than those of visible light and hence we do not see them. When the body is heated, the radiated energy corresponds to shorter wavelengths. For temperatures around 800 °C, part of the energy emitted is in the visible range and body appears *red*. At around 3000 °C, it looks *white hot*. The filament of a tungsten lamp appears white hot as its temperature is around 3000 °C

We have thus seen that all bodies radiate electromagnetic radiation when their temperature is above the absolute zero of temperature.

Amount of heat radiated by a body depends on

- The absolute temperature of the body (T)
- The nature of the body – the material, nature of surface – polished or not, etc.
- Surface area of the body (A)
- Time duration of for which body emits radiation (t)

The amount of heat radiated, Q, is directly proportional to the surface area (A) and time duration (t). It is therefore convenient to consider the quantity of heat radiated per unit area per unit time (or power emitted per unit area). This is defined as *emissive power* or *radiant power*, R, of the body, at a given temperature T.

$$\therefore R = \frac{Q}{At}$$

Dimensions of emissive power are $[L^0M^1T^{-3}]$ and SI unit is J m^{-2} s^{-1} or W/m^2.

The nature of emitting surface, i.e., its material or polishing is not a physical quantity. Hence, to discuss the material aspect, we compare objects of different materials with identical geometries at the same temperature. At a given temperature, a perfect blackbody has maximum emissive power. Thus it is convenient to compare emissive power of a given surface with that of the perfect blackbody at the same temperature.

3.12.1 Coefficient of Emission or Emissivity:

The coefficient of emission or emissivity (e) of a given surface is the ratio of the emissive power R of the surface to the emissive power R_B of a perfect black surface, at the same temperature.

$$\therefore e = \frac{R}{R_B} \qquad \text{--- (3.41)}$$

For a perfect blackbody $e = 1$, whereas for a perfect reflector $e = 0$.

Use your brain power

- Why are the bottoms of cooking utensils blackened and tops polished?
- A car is left in sunlight with all its windows closed on a hot day. After some time it is observed that the inside of the car is warmer than outside air. Why?
- If surfaces of all bodies are continuously emitting radiant energy, why do they not cool down to 0 K?

Everyday objects are not ideal blackbodies. Hence, they radiate at a rate less then that of the blackbody at the same temperature. Also for these objects, the rate does depend on properties such as the colour and composition of the surface, in addition to the temperature. All these effects together are taken care of in the term emissivity e. For an ordinary body, $0 < e < 1$ depending on the nature of the surface, e.g., emissivity of copper is 0.3. Emissivity is larger for rough surfaces and smaller for smooth and polished surfaces. Emissivity also varies with temperature and wavelength of radiation to some extent.

3.13 Kirchhoff's Law of Heat Radiation and its Theoretical Proof:

Kirchhoff's law of thermal radiation deals with wavelength specific radiative emission and absorption by a body in thermal equilibrium. It states that *at a given temperature, the ratio of emissive power to coefficient of absorption of a body is equal to the emissive power of a perfect blackbody at the same temperature for all wavelengths*.

Since we can describe the emissive power of an ordinary body in comparison to a perfect blackbody through its emissivity, Kirchhoff's law can also be stated as follows: *for a body emitting and absorbing thermal radiation in thermal equilibrium, the emissivity is equal to its absorptivity*.

Symbolically, $a = e$ or more specifically $a(\lambda) = e(\lambda)$.

Thus, if a body has high emissive power, it also has high absorptive power and if a body has low emissive power, it also has low absorptive power.

Kirchhoff's law can be theoretically proved by the following thought experiment. Consider an ordinary body A and a perfect blackbody B of identical geometric shapes placed in an enclosure. In thermal equilibrium, both bodies will be at same temperature as that of the enclosure.

Let R be the emissive power of body A, R_B be the emissive power of blackbody B and a be the coefficient of absorption of body A. If Q is the quantity of radiant heat incident on each body in unit time and Q_a is the quantity of radiant heat absorbed by the body A, then $Q_a = a\,Q$. As the temperatures of the body A and blackbody B remain the same, both must emit the same amount as they absorb in unit time. Since emissive power is the quantity of heat radiated from unit area in unit time, we can write

Quantity of radiant heat absorbed by body A= Quantity of heat emitted by body A or, $a\,Q = R$ --- (3.42)

For the perfect blackbody B,

$$Q = R_B \quad \text{--- (3.43)}$$

Dividing Eq. (3.42) by Eq.(3.43), we get

$$a = \frac{R}{R_B}$$

$$\text{or,} \quad \frac{R}{a} = R_B \quad \text{--- (3.44)}$$

But $\frac{R}{R_B} = e$ from Eq. (3.41), $\therefore\ a = e$.

Hence, Kirchhoff's law is theoretically proved. Can you give two applications of Kirchhoff's law in daily life?

3.14 Spectral Distribution of Blackbody Radiation:

The radiant energy emitted per unit area per unit time by a blackbody depends on its temperature. Hot objects radiate electromagnetic radiation in a large range of frequencies. Hence, the rate of emission per unit area or power per unit area of a surface is defined as a funtion of the wavelength λ of the emitted radiation. At low temperature, the power radiated is small and primarily lies in the long wavelength region. As the temperature is increased, rate of emission increases fast. At each temperature, the radiant energy contains a mixture of different wavelengths. At higher temperatures, the total energy radiated per unit time increases and the proportion of energy emitted at higher frequencies or shorter wavelengths also increases.

Lummer and Pringsheim studied the energy distribution of blackbody radiation as a function of wavelength. They kept the source of radiation (such as a cavity radiator) at different temperatures and measured the radiant power corresponding to different wavelengths. The measurements were represented graphically in the form of curves showing variation of radiant power per unit area as a function of wavelength λ at different constant temperatures as shown in Fig. 3.5. Spectral distribution of power radiated by a body indicates the power radiated at different wavelengths. Experimental observations indicated that the spectral distribution depended only on the absolute temperature *T* of a blackbody and was independent of the material.

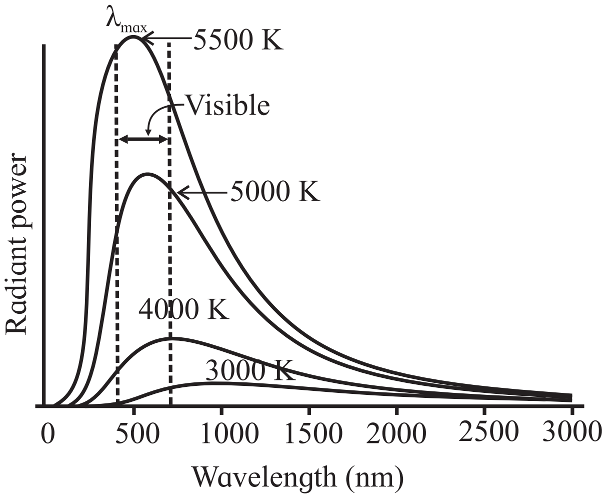


Fig. 3.5: Radiant power of a blackbody per unit range of wavelength as a function of wavelength.

From experimental curves, it is observed that

1. at a given temperature, the energy is not uniformly distributed in the spectrum (i.e., as a function of wavelength) of blackbody,
2. at a given temperature, the radiant power emitted initially increases with increase of wavelength, reaches it's maximum and then decreases. The wavelength corresponding to the radiation of maximum intensity, λ_{max}, is characteristic of the temperature of the radiating body. (Remember, it is not the *maximum wavelength* emitted by the object),
3. area under the curve represents total energy emitted per unit time per unit area by the blackbody at all wavelengths,
4. the peak of the curves shifts towards the left – shorter wavelengths, i.e., the value of λ_{max} decreases with increase in temperature,
5. at higher temperatures, the radiant power or total energy emitted per unit time per unit area (i.e., the area under the curve)

corresponding to all the wavelengths increases,

6. at a temperature of 300 K (around room temperature), the most intense of these waves has a wavelength of about 5×10^{-5} m; the radiant power is smaller for wavelengths other than this value. Practically all the radiant energy at this temperature is carried by waves longer than those corresponding to red light. These are infrared radiations.

A theoretical explanation of the above observations could not be given by the then existing theories. Wien gave an expression for spectral distribution from laws of thermodynamics, which fitted the experimental observations only for short wavelengths. Lord Rayleigh and Sir James Jeans gave a formula from the equipartition of energy. This formula fits well in the long wavelength regions but tends to infinity at short wavelengths. It was therefore essential to propose a new model to explain the behaviour of blackbody. Planck, being aware of the shortcomings of the two models, combined the two models using an empirical formula and could describe the observed spectrum quite well.

Do you know?

The idea of quantization of energy was first proposed by Planck to explain the blackbody spectrum or the cavity radiations. Planck proposed a model in terms of the atomic processes. He considered the atoms of the walls of the cavity as tiny electromagnetic oscillators with characteristic frequencies that exchange energy with the cavity. This energy was supposed to have only specific values $E = nh\nu$, where ν is the frequency of oscillator, h is a universal constant that has a value 6.626×10^{-34} J s and n can take only positive integral values. The oscillators would not radiate energy continuously but only in "jumps" or "quanta" corresponding to transitions from one quantized level of energy to another of lower energy. As long as the oscillator is in one of the quantized states, it does not emit or absorb energy. This model of Planck turned out to be the basis for Einstein's theory to explain the observations of experiments on photoelectric effect, as you will learn in Chapter 14.

3.14.1 Wien's Displacement Law :

It is observed that the wavelength, for which emissive power of a blackbody is maximum, is inversely proportional to the absolute temperature of the blackbody. This is Wien's displacement law.

$$\lambda_{\max} \propto \frac{1}{T}$$

$$\text{or,} \quad \lambda_{\max} = \frac{b}{T}$$

$$\therefore \lambda_{\max} T = b \qquad \text{--- (3.45)}$$

where b is called the Wien's constant and its value is 2.897×10^{-3} m K. λ_{max} indicates the wavelength at which the blackbody dominantly radiates. Thus, it corresponds to the dominant colour of the radiating body and is a function of its temperature. You might have heard of white dwarfs and red giants, white dwarfs are hot stars with surface temperature ~ 10000 K while red giants are cooler corresponding to surface temperature ~ 3000 K.

This law is useful to determine temperatures of distant stars, Sun, moon etc.

Example 3.5: Calculate the value of $\lambda_{\max}$ for solar radiation assuming that surface temperature of Sun is 5800 K ($b = 2.897 \times 10^{-3}$ m K). In which part of the electromagnetic spectrum, does this value lie?

Solution: Given

T = 5800 K and b = 2.897×10^{-3} m K.

Using Eq. (3.45),

$$\lambda_{\max} = \frac{2.897 \times 10^{-3}\ \text{m K}}{5800\,\text{K}}$$

$$= 4.995 \times 10^{-7}\,\text{m} = 4995\ \text{Å}.$$

This value lies in the visible region of the electromagnetic spectrum.

Can you tell?

λ_{max}, the wavelength corresponding to maximum intensity for the Sun is in the blue-green region of visible spectrum. Why does the Sun then appear yellow to us?

33.15 Stefan-Boltzmann Law of Radiation:

We shall now discuss the temperature dependence of thermal radiation emitted per unit time by a blackbody. In 1879, Josef Stefan proposed an empirical relation between the rate at which heat is radiated (the radiant power R) from unit area of a perfect blackbody and its temperature T, based on the experimental observations. Five years later, Boltzmann derived the relation using thermodynamics. Hence it is known as Stefan-Boltzmann law. According to this law,"*The rate of emission of radiant energy per unit area or the power radiated per unit area of a perfect blackbody is directly proportional to the fourth power of its absolute temperature*".

$$R \propto T^4$$

$$\text{or, } R = \sigma T^4 \qquad \text{--- (3.46)}$$

where σ is Stefan's constant and is equal to 5.67×10^{-8} J m^{-2} s^{-1} K^{-4} or W m^{-2} K^{-4} and dimensions of σ are $[L^0M^1T^{-3}K^{-4}]$.

Thus, the power radiated by a perfect blackbody depends only on its temperature and not on any other characteristics such as colour, materials, nature of surface etc.

If Q is the amount of radiant energy emitted in time t by a perfect blackbody of surface area A at temperature T, then $\dfrac{Q}{At} = \sigma T^4$.

For a body, which is not a blackbody, the energy radiated per unit area per unit time is still proportional to the fourth power of temperature but is less than that for the blackbody. For an ordinary body,

$$R = e\sigma T^4 \qquad \text{--- (3.47)}$$

where e is emissivity of the surface.

If the perfect blackbody having absolute temperature T is kept in a surrounding which is at a lower absolute temperature T_0, then the energy radiated per unit area per unit time $= \sigma T^4$

Energy absorbed from surroundings per unit area per unit time $= \sigma T_0^4$

Therefore net loss of energy by perfect blackbody per unit area per unit time $= \sigma T^4 - \sigma T_0^4 = \sigma(T^4 - T_0^4)$.

For an ordinary body, at temperature T, net loss of energy per unit area per unit time $= e\sigma\left(T^4 - T_0^4\right)$.

On the other hand, if the body is at a temperature lower than the surrounding i.e., $T < T_0$, then $e\sigma\left(T_0^4 - T^4\right)$ will be the net gain in thermal energy of the body per unit area per unit time.

Since the loss or gain of energy per unit area per unit time is proportional to the fourth power of absolute temperature, this law is very significant in deciding the thermal equilibrium of physical systems. If the absolute temperature of a body is doubled, the power radiated will increase by a factor of $2^4 = 16$. Or if a body radiates with some rate at room temperature (300 K), the rate will double even if we increase the temperature of the body by 57 °C.

Example 3.6: Calculate the energy radiated in one minute by a blackbody of surface area 200 cm^2 at 127 °C ($\sigma = 5.67 \times 10^{-8}$J m^{-2} s^{-1} K^{-4}).

Solution: Given

$A = 200$ cm^2 $= 200 \times 10^{-4}$ m^2,

$T = 127$ °C $= (127+273)$ K $= 400$ K,

$t = 1$ min $= 60$ s

We know that energy radiated is given by

$$Q = \sigma\, AtT^4$$

$= 5.7 \times 10^{-8} \times 200 \times 10^{-4} \times 60 \times (400)^4$

$= 5.7 \text{ x } 1.2 \text{ x } 256$

$= 1742$ J

Example 3.7: A 60 watt filament lamp loses all its energy by radiation from its surface. The emissivity of the surface is 0.5. The area of the surface is 5×10^{-5} m^2. Find the temperature of the filament ($\sigma = 5.67 \times 10^{-8}$J m^{-2} s^{-1} K^{-4}).

Solution: Given, $e = 0.5$, $A = 5 \times 10^{-5}$ m^2,

$\frac{dQ}{dt} = 60$ W $= 60$ J s^{-1}

We know that $\frac{dQ}{dt} = e\sigma A T^4$

$\therefore 60 = 0.5 \times 5.67 \times 10^{-8} \times 5 \times 10^{-5} \times T^4$

$$\therefore T^4 = \frac{60 \times 10^{13}}{5.67 \times 2.5}$$

$T^4 = 4.23 \times 10^{13}$

$$\therefore T = \left(42.3 \times 10^{12}\right)^{1/4}$$

$T = 2.55 \times 10^3 = 2550$ K

Example 3.8: Compare the rate of loss of heat from a metal sphere at 827 °C with the rate of loss of heat from the same sphere at 427 °C, if the temperature of the surrounding is 27 °C.

Solution: Given,

$T_1 = 827$ °C $= 827 + 273 = 1100$ K,

$T_2 = 427$ °C $= 427 + 273 = 700$ K and

$T_0 = 27$ °C $= 27 + 273 = 300$ K

$$R_1 = \left(\frac{dQ}{dt}\right)_1 = e\sigma A\left(T_1^4 - T_0^4\right)$$

$$R_2 = \left(\frac{dQ}{dt}\right)_2 = e\sigma A\left(T_2^4 - T_0^4\right)$$

$$\therefore \frac{R_1}{R_2} = \frac{\left(T_1^4 - T_0^4\right)}{\left(T_2^4 - T_0^4\right)} = \frac{1100^4 - 300^4}{700^4 - 300^4}$$

$$\text{or,} \quad \frac{R_1}{R_2} = \frac{14560}{2320} = \frac{182}{29}$$

$$\therefore R_1 : R_2 = 182 : 29$$

Example 3.9: Assuming that the temperature at the surface of the Sun is 6000 K, find out the size of a virtual star (in terms of the size of Sun) whose surface temperature is 3000 K and the power radiated by the virtual star is 25 times the power radiated by the Sun. Treat both, the Sun and virtual star as a blackbody.

Solution: Given,

$T_{\text{Sun}} = 6000$ K,

$T_{\text{star}} = 3000$ K,

$P_{\text{star}} = 25 \times P_{\text{Sun}}$

Power radiated by the Sun

$$= P_{\text{Sun}} = \left(\frac{dQ}{dt}\right)_{\text{Sun}} = \sigma A_{\text{Sun}} T_{\text{Sun}}^4 = \sigma 4\pi r_{\text{Sun}}^2 T_{\text{Sun}}^4$$

Power radiated by the virtual star

$$= P_{\text{star}} = \left(\frac{dQ}{dt}\right)_{\text{star}} = \sigma A_{\text{star}} T_{\text{star}}^4 = \sigma 4\pi r_{\text{star}}^2 T_{\text{star}}^4$$

$$\therefore \frac{P_{\text{star}}}{P_{\text{Sun}}} = \frac{\sigma 4\pi r_{\text{star}}^2 T_{\text{star}}^4}{\sigma 4\pi r_{\text{Sun}}^2 T_{\text{Sun}}^4} = \frac{r_{\text{star}}^2\, 3000^4}{r_{\text{Sun}}^2\, 6000^4} = 25$$

$$\therefore \frac{r_{\text{star}}^2}{r_{\text{Sun}}^2} = 25 \times \frac{6000^4}{3000^4} = 400$$

or, $r_{\text{star}} = 20 \times r_{\text{Sun}}$

Internet my friend

- https://www.britannica.com/science/kinetic-theory-of-gases
- https://www.youtube.com/watch?v=XrAktUy3_3k
- https://www.youtube.com/watch?v=3tD7ZuqaZik
- https://www.youtube.com/watch?v=7BXvc9W97iU
- https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Map%3A_Physical_Chemistry_(McQuarrie_and_Simon)/01%3A_The_Dawn_of_the_Quantum_Theory/1.01%3A_Blackbody_Radiation_Cannot_Be_Explained_Classically
- http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/kinthe.html
- https://www.youtube.com/watch?v=Qsa4aAdpHfy
- https://www.youtube.com watch?v=buPuKAcKqZw

Exercises

1. Choose the correct option.

i) In an ideal gas, the molecules possess
(A) only kinetic energy
(B) both kinetic energy and potential energy
(C) only potential energy
(D) neither kinetic energy nor potential energy

ii) The mean free path λ of molecules is given by
(A) $\sqrt{\frac{2}{\pi n d^2}}$ (B) $\frac{1}{\pi n d^2}$
(C) $\frac{1}{\sqrt{2}\pi n d^2}$ (D) $\frac{1}{\sqrt{2}\pi n d}$,
where n is the number of molecules per unit volume and d is the diameter of the molecules.

iii) If pressure of an ideal gas is decreased by 10% isothermally, then its volume will
(A) decrease by 9%
(B) increase by 9%
(C) decrease by 10%
(D) increase by 11.11%

iv) If $a = 0.72$ and $r = 0.24$, then the value of t_r is
(A) 0.02 (B) 0.04 (C) 0.4 (D) 0.2

v) The ratio of emissive power of a perfect blackbody at 1327° C and 527° C is
(A) 4:1 (B) 16 : 1 (C) 2 : 1 (D) 8 : 1

2. Answer in brief.

i) What will happen to the mean square speed of the molecules of a gas if the temperature of the gas increases?

ii) On what factors do the degrees of freedom depend?

iii) Write ideal gas equation for a mass of 7 g of nitrogen gas.

iv) What is an ideal gas ? Does an ideal gas exist in practice ?.

v) Define athermanous substances and diathermanous substances.

3. When a gas is heated its temperature increases. Explain this phenomenon based on kinetic theory of gases.

4. Explain, on the basis of kinetic theory, how the pressure of gas changes if its volume is reduced at constant temperature.

5. Mention the conditions under which a real gas obeys ideal gas equation.

6. State the law of equipartition of energy and hence calculate molar specific heat of mono- and di-atomic gases at constant volume and constant pressure.

7. What is a perfect blackbody ? How can it be realized in practice?

8. State (i) Stefan-Boltmann law and (ii) Wein's displacement law.

9. Explain spectral distribution of blackbody radiation.

10. State and prove Kirchoff's law of heat radiation.

11. Calculate the ratio of mean square speeds of molecules of a gas at 30 K and 120 K.

[Ans: 1:4]

12. Two vessels A and B are filled with same gas where volume, temperature and pressure in vessel A is twice the volume, temperature and pressure in vessel B. Calculate the ratio of number of molecules of gas in vessel A to that in vessel B.

[Ans: 2:1]

13. A gas in a cylinder is at pressure P. If the masses of all the molecules are made one third of their original value and their speeds are doubled, then find the resultant pressure.

[Ans: 4/3 P]

14. Show that rms velocity of an oxygen molecule is $\sqrt{2}$ times that of a sulfur dioxide molecule at S.T.P.

15. At what temperature will oxygen molecules have same rms speed as helium molecules at S.T.P.? (Molecular masses of oxygen and helium are 32 and 4 respectively)

[Ans: 2184 K]

16. Compare the rms speed of hydrogen molecules at 127 °C with rms speed of oxygen molecules at 27 °C given that molecular masses of hydrogen and oxygen are 2 and 32 respectively.

[Ans: 8: $\sqrt{3}$]

17. Find kinetic energy of 5000 cc of a gas at S.T.P. given standard pressure is 1.013 × 10^5 N/m^2.

[Ans: 7.598 × 10^2 J]

18. Calculate the average molecular kinetic energy (i) per kmol (ii) per kg (iii) per molecule of oxygen at 127 °C, given that molecular weight of oxygen is 32, R is 8.31 J mol^{-1} K^{-1} and Avogadro's number N_A is 6.02 x 10^{23} molecules mol^{-1}.

[Ans: 4.986 × 10^6 J, 1.558 × 10^2 J
8.282 × 10^{-21} J]

19. Calculate the energy radiated in one minute by a blackbody of surface area 100 cm^2 when it is maintained at 227 °C. (Take Stefen's constant

$\sigma = 5.67 \times 10^{-8}$ J $m^{-2}s^{-1}K^{-4}$)

[Ans: 2126.25 J]

20. Energy is emitted from a hole in an electric furnace at the rate of 20 W, when the temperature of the furnace is 727 °C. What is the area of the hole? (Take Stefan's constant σ to be 5.7 × 10^{-8} J s^{-1} m^{-2} K^{-4})

[Ans: 3.509 × 10^{-4} m^2]

21. The emissive power of a sphere of area 0.02 m^2 is 0.5 kcal s^{-1} m^{-2}. What is the amount of heat radiated by the spherical surface in 20 second?

[Ans: 0.2 kcal]

22. Compare the rates of emission of heat by a blackbody maintained at 727 °C and at 227 °C, if the blackbodies are surrounded by an enclosure (black) at 27 °C. What would be the ratio of their rates of loss of heat ?

[Ans: 18.23:1]

23. Earth's mean temperature can be assumed to be 280 K. How will the curve of blackbody radiation look like for this temperature? Find out λ_{max}. In which part of the electromagnetic spectrum, does this value lie? (Take Wien's constant b = 2.897 × 10^{-3} m K)

[Ans: 1.035 × 10^{-5} m, infrared region]

24. A small-blackened solid copper sphere of radius 2.5 cm is placed in an evacuated chamber. The temperature of the chamber is maintained at 100 °C. At what rate energy must be supplied to the copper sphere to maintain its temperature at 110 °C? (Take Stefan's constant σ to be 5.670 × 10^{-8} J s^{-1} m^{-2} K^{-4}, π = 3.1416 and treat the sphere as a blackbody.)

[Ans: 0.9624 W]

25. Find the temperature of a blackbody if its spectrum has a peak at (a) λ_{max} = 700 nm (visible), (b) λ_{max} = 3 cm (microwave region) and (c) λ_{max} = 3 m (short radio waves) (Take Wien's constant b = 2.897 × 10^{-3} m K).

[Ans: (a) 4138 K, (b) 0.09657 K,
(c) 0.9657 × 10^{-3} K]

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