
UNIT 2 THERMAL ENERGY

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2.1 INTRODUCTION

In Unit 1, you studied some important properties of matter such as hydrostatic pressure, viscosity and elasticity. The knowledge of these parameters is very useful in selection of materials for construction and manufacturing industries. Moreover, from engineering point of view, thermal behaviour of matter is also of great importance. Even in our day-to-day life, thermal energy plays a crucial role. For example, thermal energy from the sun sustain life on our planet. The invention of heat engines has made a significant contribution to the industrial progress of the society. It is, therefore, important for you to understand the concept of thermal energy and other phenomenon related to heat. This is the subject matter of the present unit.

In our common language, we use the terms heat, temperature and thermal energy almost interchangeably. This is not correct from physics point of view; each of these terms have a precise meaning. You will learn what these terms refer to and what are the subtle differences among them in Section 2.2. After having discovered that heat is a form of energy in transit, scientists tried to measure it in terms of mechanical parameters. Joule showed experimentally that the heat energy can be quantified in terms of mechanical work and you will learn the details of this experiment in Section 2.3.

In Section 2.4, you will discover answers to question, related to the transport of heat energy from one body to another, such as : How does heat travel? Is there only one mode of transport of heat from one body to another and from one place to another? What happens when water is heated?

The understanding of relation between the thermal energy and motion of the microscopic particles of matter was developed on the basis of the kinetic theory of gases. This theory gained wider acceptability by predicting experimentally

verifiable gas laws. You will learn the basics of the kinetic theory of gases in Section 2.5.

Objectives

After studying this unit, you should be able to

- state the zeroth law of thermodynamics and explain the concept of temperature,
- describe Joule's experiment and state its significance,
- explain the transfer of heat through conduction, convection and radiation,
- state the laws governing the behaviour of thermal radiations,
- state the basic assumption of the kinetic theory of gases,
- derive an expression for the pressure exerted by an ideal gas, and
- derive various gas laws on the basis of the kinetic theory of gases.

2.2 WHAT IS HEAT?

Our understanding of heat is intimately linked on the notion of temperature. For example, **hot** corresponds to higher temperature than **cold**. Similarly, higher the temperature of our body, greater is the (sensation of) heat. However, the sensations of hot and cold are subjective perceptions and do not help in giving a precise meaning to heat or temperature.

The recognition of heat as a form of energy (thermal energy) comes from the principle of conservation of energy. You know that, according to this principle, energy can only be converted from one form to another and that the energy is conserved. So, in winter, when we rub our palms to get the sensation of warmth, mechanical (frictional) energy is converted into heat energy. On the other hand, the heat engines convert thermal energy into mechanical energy. The intimate relation between the heat and mechanical energies enables us to define heat and thermal energy in terms of the motion of the microscopic particles in the matter. *Thermal energy of a system is defined as the average translational kinetic energy of its particles. Temperature is a measure of the translational kinetic energy of the system and heat is the flow of thermal energy from a system at higher temperature to a system (or surrounding) at lower temperature.* We shall discuss the kinetic interpretation of thermal energy in greater detail later in this unit.

To further elaborate the concept of heat, consider a simple experiment. Let a beaker, filled with water, is kept above the flame of a gas stove. After sometime, the temperature of water increases. The rise in temperature or the *heating of water is because of the transfer of (thermal) energy from the flame to the water*. Also, the transfer of energy occurs because there is a difference in temperature between the flame and the water. **Thus, we define heat as energy transferred from one object to another by virtue of a temperature difference.** From this definition, the following two things are obvious :

- (a) the characteristic feature of heat is that it is transferred between two objects only when there exists a temperature difference between them; and

- (b) an object does not possess heat; heat is a form of energy rather than a substance.

The SI unit of heat energy is **Joule** and the practical unit of heat energy is **calorie**. *One calorie of heat is defined as the amount of heat energy required to raise the temperature of one gram of water through 1°C .* The relation between Joule and calorie is :

$$1 \text{ calorie} = 4.186 \text{ Joules}$$

As evident from the above discussion, temperatures of two bodies determine the direction of flow of heat from one body to another. **In other words, we can say that temperature is a physical parameter of a body which quantifies our subjective sense of hot and cold.** To explain this parameter further, you need to know the concept of thermal equilibrium and the zeroth law of thermodynamics.

2.2.1 Thermal Equilibrium and Zeroth Law

If two bodies at different temperatures are placed in thermal contact with one another and are thermally isolated from their surroundings (Figure 2.1), both the bodies will be at the same temperature after a certain time. **When two bodies are at the same temperature, they are said to be in thermal equilibrium.**

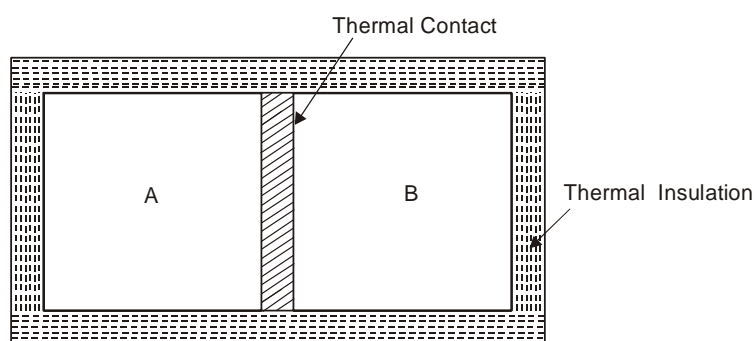


Figure 2.1 : Two Bodies A and B in Thermal Contact

Further, even if two bodies or systems are not in thermal contact with each other, they can be in thermal equilibrium. To understand how this is possible, consider two systems A and B, which are thermally insulated from each other. Now, if these two systems are placed in thermal contact with a third system C (Figure 2.2), both of them will separately attain thermal equilibrium with the

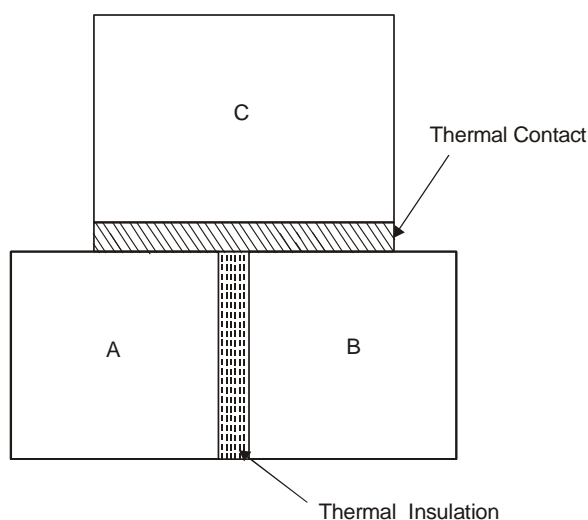


Figure 2.2 : Two Thermally Isolated Systems A and B are in Thermal Contact with a Third System C

system *C*. Moreover, it has been observed experimentally that under this condition, system *A* and *B* are also in thermal equilibrium with each other. This experimental finding is known as the **zeroth law of thermodynamics** and is formally stated as : *Two systems, each in thermal equilibrium separately with a third system, are also in thermal equilibrium with each other.*

Temperature and its Measurement

The concept of thermal equilibrium enables us to measure temperature. When two systems at different temperatures are placed in thermal contact with each other, they attain thermal equilibrium with passage of time and their temperatures become the same. If one of these two systems is a **thermometer**, we can determine the temperature of the other system.

Thermometer is a device which measures temperature dependent properties of matter. For example, in a common clinical thermometer, expansion of mercury is measured. Another requirement for temperature measurement is to *define a temperature scale*. An empirical recipe for defining the temperature scale is to select two '**fixed points**' corresponding to reproducible temperatures. A convenient choice of the fixed points are the melting point of ice and the boiling point of water at atmospheric pressure. These fixed points are spaced out by a convenient number of subdivisions each of which is called a 'degree' ($^{\circ}$). *Common temperature measurements relies on the Celsius (C) and Fahrenheit (F) scales and the fixed points on these two scales are divided respectively into 100 degree Celsius and 212 degree Fahrenheit.* Therefore, the readings on one of these two scales can be converted into another by using the following relation :

$$C = (F - 32) \frac{5}{9}$$

$$\text{or,} \quad F = \left(\frac{9}{5} C \right) + 32 \quad \dots (2.1)$$

However, in the modern scientific works, we use **Kelvin** (or **absolute**) scale of temperature where temperature is measured relative to an arbitrarily chosen fixed point called '*triple point of water*'. This fixed point refers to the state where pure water coexists as a mixture of ice, liquid and vapour. The temperature at which this state exists has arbitrarily been assigned the value of 273.16 Kelvin, written as 273.16 K, and this state is also called the 'standard fixed point'. The Kelvin scale and the Celsius scale are related to each other by the fact that the triple point of water is defined to be exactly at 0.01°C and a temperature difference of 1 K is equal to a temperature difference of 1°C . Thus, we have the conversion relation between Kelvin and Celsius scales as :

$$K = C + 273.15 \quad \dots (2.2)$$

When heat is added to a system, its temperature rises. However, it is observed that some systems (materials) require more heat than other systems to make their temperatures rise by a given amount or, equivalently, when a fixed amount of heat is given to fixed masses of different substances, the rise in temperatures are different. These observations could be understood in terms of a physical parameter called heat capacity of materials. You will learn it now. Before this, let us solve an SAQ.

At what temperature is the numerical value same on both the Celsius and Fahrenheit scales?

2.2.2 Specific Heat Capacity

If the temperature of a system changes by an amount ΔT due to transfer of heat Q into or from the system, heat capacity C of the system is defined as :

$$C = \frac{Q}{\Delta T} \quad \dots (2.3)$$

The unit of heat capacity is Joules per Kelvin (JK^{-1}). Since the amount of heat absorbed by a system for producing a given change in temperature depends on the mass m of the system, we define a parameter called the **specific heat capacity** as :

$$c = \frac{C}{m} \quad \dots (2.4)$$

If $\Delta T = 1$ and $m = 1$, we have $c = Q$. Thus, *specific heat capacity of a substance may be defined as the amount of heat required to raise the temperature of unit mass of the substance through unit degree*. Yet another related parameter which defines heat capacity in terms of microscopic parameters is called **molar heat capacity** and is given as :

$$\text{Molar heat capacity} = \frac{C}{n} \quad \dots (2.5)$$

where n is the number of moles (written in the abbreviated form as “mol”). Therefore, *molar heat capacity is the amount of heat required to raise the temperature of one mole of the substance through a unit degree*. The molar heat capacity is measured in $\text{J mol}^{-1}\text{K}^{-1}$.

[Note : 1 mole of any substance contains a fixed number, called Avogadro’s number ($N_A = 6.02 \times 10^{23}$) of atoms/molecules. However, weights of 1 mole of different substances are different. The weight of 1 mole of a substance is equal to its atomic mass in grams. That is, the weight of 1 mole of oxygen is 16 grams because the atomic mass of oxygen is 16.]

The value of heat capacity depends on the process of heat transfer. If transfer of heat takes place keeping pressure of the system constant, C is called the *heat capacity at constant pressure* and is denoted by the symbol C_p . Mathematically :

$$C_p = \left(\frac{Q}{\Delta T} \right)_p \quad \dots (2.6)$$

Similarly, the *heat capacity at constant volume*, C_v is expressed as :

$$C_v = \left(\frac{Q}{\Delta T} \right)_v \quad \dots (2.7)$$

Till now, you studied the nature of heat and its relation with temperature. You know from day-to-day experience that there is some kind of relation between heat and mechanical work. British physicist James P. Joule carried out a variety of experiments to investigate the relation between these two physical parameters. You will now learn the details of the Joule's experiment and the notion of mechanical equivalent of heat.

However, to check your understanding of what you have learnt in this section, you should solve the following SAQs.

SAQ 2



- (a) A copper calorimeter weighing 250 g is at temperature 20°C. When 50 g of water at 30°C is poured into the calorimeter cup, the temperature of the cup-water system becomes 26.8°C. Calculate the specific heat capacity of the cup.
- (b) Having determined the specific heat capacity of the copper calorimeter in (a) above, you can determine the specific heat of other materials. Suppose a 300 g block of aluminium is raised to a temperature of 100°C by placing it in the steam (boiling water) at atmospheric pressure. This block of aluminium is quickly placed into the calorimeter, which contains 400 g of water at an initial temperature of 20°C. The aluminium block, the copper calorimeter, and the water come to a final common temperature of 30.4°C. Calculate the specific heat capacity of aluminium.

2.3 MECHANICAL EQUIVALENT OF HEAT

Through a series of experiments, Joule established that the temperature of a given system or substance can be raised by any one of the following two methods :

- (a) by supplying heat, and
- (b) by doing mechanical work.

On the basis of these observations, he concluded that both these processes are equivalent. This gave rise to the notion of *mechanical equivalent of heat*.

To establish a quantitative relationship between the amount of heat generated and the amount of work done, Joule devised an apparatus in which water in a vessel was stirred vigorously by a set of rotating paddles. The mechanical energy supplied to rotate the paddles could be accurately measured. And, at the same time, the heat generated in the process could also be calculated in terms of the rise in temperature of the water and a knowledge of the heat capacities of water, the paddles, and the vessel.

Experiments done by Joule showed that whenever a certain amount of mechanical work (W) is done, an equivalent amount of heat (Q) is always produced. That is :

$$W \propto Q$$

Using J as the constant of proportionality, called **Joule's mechanical equivalent of heat**, we can write :

$$W = J Q$$

or, $J = \frac{W}{Q} \quad \dots (2.8)$

If $Q = 1$, then $J = W$. Therefore, *Joule's mechanical equivalent of heat can be defined as the amount of work done to produce a unit quantity of heat*. Its value is 4.186 J cal^{-1} . In SI units, both Q and W are measured in Joule. You may note that Joule's experiment showed that both work and heat are two equivalent forms of energy. Let us now discuss the experimental set up of this pioneering experiment done by Joule.

2.3.1 Joule's Experiment

The experimental arrangement used by Joule to determine the value of J is shown in Figure 2.3. It consists of a cylindrical copper calorimeter covered with a water-tight lid. In the inner wall of the calorimeter, inner vanes (V) are fixed. The spindle (S) which carries paddles (P) passes through a central hole in the lid of the calorimeter. These paddles rotate in the openings between the fixed vanes. The drum (D) is connected with the spindle through a pin N . The spindle can be disconnected by removing the pin N . A hand (H) is fixed at the top of the drum. Two equal masses (each of mass M) are attached at the ends of the string that passes over frictionless pulleys P_1 and P_2 and are then wound on the drum D . The two meter scales are used vertically to measure the heights through which the masses fall. To measure the temperature of water, a sensitive thermometer (T) is fixed in a non-central hole in the lid of thermometer.

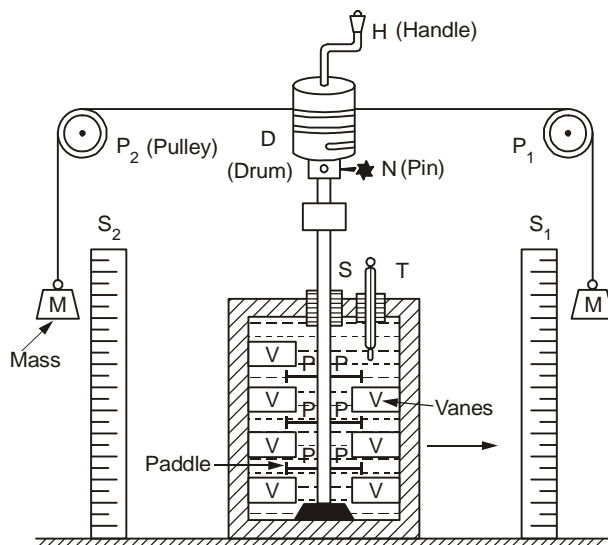


Figure 2.3 : Experimental Set-up for the Joule's Method

Working

Water (mass m) is put in the calorimeter and its temperature is noted. The masses M, M are allowed to fall freely from the same height h . This causes the spindle and the paddles to rotate and thereby churn the water in the calorimeter. The vanes try to prevent the churning motion of water. But the potential energy of the masses is used up in overcoming the friction due to vanes. This leads to the production of heat and hence there is an increase in temperature of water. Thus, the potential energy of the masses is first converted into kinetic energy of water and finally into heat energy.

When the masses are about to reach the ground, the pin N is removed. As a result, the spindle is quickly disconnected from the drum. The cords are quickly wound on the drum with the help of the handle till the masses are raised to their original level. The spindle is again connected to the drum with the help of the pin N and masses are once again allowed to fall.

In this way, the masses are allowed to fall many times till there is a measurable increase in the temperature of water. The final temperature of water and the total height through which the masses fall are also noted.

Calculations

Suppose W be the water equivalent of the calorimeter (calorimeter, spindle, paddles and vanes), $(T_2 - T_1)$ °C is the rise in temperature of water, m g is the mass of water in the calorimeter, M g is the mass of each suspended weight, h cm is the height through which each mass falls, g is the acceleration due to gravity and n is the number of times the masses falls. Therefore, we can write :

Work done by the two masses, each of mass M , in one fall

$$= 2 M g h \text{ ergs}$$

Total work done in n falls,

$$W = 2 M g h \times n \text{ ergs}$$

Amount of heat produced,

$$Q = (m + W) (T_2 - T_1) \text{ calorie}$$

(Assuming that the specific heat capacity of water is one.)

Thus, we have the Joule's constant,

$$J = \frac{W}{Q}$$

$$= \frac{2 M g h \times n}{(m + W) (T_2 - T_1)} \text{ erg.cal}^{-1}$$

Result

The value of J obtained by this experiment is $4.15 \times 10^7 \text{ erg cal}^{-1}$.

However, the most accurate value of J is $4.186 \times 10^7 \text{ erg cal}^{-1}$. The discrepancy in the values of J is due to some *sources of error* as mentioned below :

- (a) A part of the potential energy is converted into kinetic energy of the falling masses.
- (b) A part of the potential energy of the falling masses is also used up to overcome the friction in pulleys and other parts of the apparatus.
- (c) As the temperature of the calorimeter is higher than that of its surroundings, there is a transfer of heat between the two. So, the observed value of final temperature is slightly less than what it should be.

You have studied that whenever two objects in thermal contact with each other are not in thermal equilibrium, there is a transfer of heat energy. You also know that heat is the form of energy which is transferred between two objects solely because a temperature difference exists between them. Now, the next logical question is : **How does the transfer of heat energy takes place?** You will learn it now.

But before proceeding further, how about solving an SAQ?

SAQ 3



A mass of 5 kg falls through a height of 40 m and rotate a paddle wheel which churns 0.5 kg of water. The initial temperature of water is 1.5°C . Calculate the increase in the temperature. (Given : $J = 4.2 \times 10^7 \text{ erg}\cdot\text{cal}^{-1}$.)

2.4 MODES OF HEAT TRANSFER

Transfer of heat from one system (object) to another or from an object to its surroundings takes place through one of the three modes/processes namely, conduction, convection and radiation. Let us now discuss these processes and related concepts.

2.4.1 Conduction

In the conduction process, heat is transferred from one body to another through a connecting medium. For example, when we hold a metal bar whose other end is heated, heat is transferred from the flame to our hand due to conduction through the metal bar, the connecting medium (Figure 2.4). Conduction is also characterized by the fact that there is no flow of matter. A physical parameter associated with conduction is called thermal conductivity. Let us learn it now.

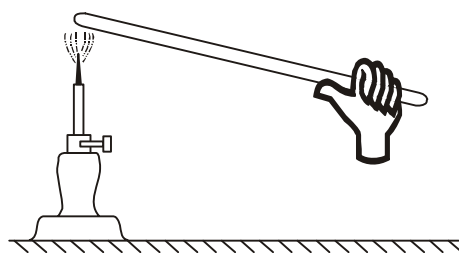


Figure 2.4 : Transfer of Heat due to Conduction

Thermal Conductivity

Thermal conductivity is an important parameter of materials and it indicates how fast the transfer of heat can take place. It enables us to select materials for a variety of purposes such as thermal insulation.

To obtain an expression for thermal conductivity, let us consider a piece of material made in the form of a slab of thickness Δx and area A (Figure 2.5). One of two opposite faces is maintained at temperature T and the other at

$T + \Delta T$ (hot face). The heat ΔQ that flows perpendicular to the faces during the time interval Δt is measured. The experiment is repeated with other slabs of the same material having different set of values of Δx and A . It is found that :

- (a) for a given ΔT , ΔQ is proportional to Δt and A , and
- (b) for a given Δt and A , ΔQ is proportional to the ratio $\frac{\Delta T}{\Delta x}$,
provided that both ΔT and Δx are small.

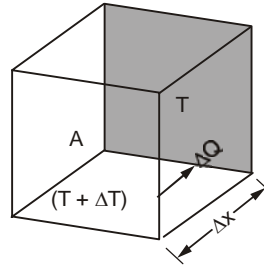


Figure 2.5 : Heat Flow in a Slab whose Two Faces are at Different Temperatures

Thus, we can write :

$$\Delta Q \propto A \Delta t \frac{\Delta T}{\Delta x}$$

Above expression can be written in the generalized form as :

$$\frac{dQ}{dt} = -KA \frac{dT}{dx} \quad \dots (2.9)$$

The term $\frac{dQ}{dt}$ in Eq. (2.9) is called **heat current** and the spatial derivative of temperature, $\frac{dT}{dx}$ is called the **temperature gradient**. The negative sign in Eq. (2.9) indicates that the heat flows in the direction of decreasing temperature, that is, in the direction along which $\frac{dT}{dx}$ is negative. The constant of proportionality, K , is called the **thermal conductivity** which relates the rate of heat flow per unit area to the magnitude of the temperature gradient $\left(\frac{\Delta T}{\Delta x}\right)$.

You may note from Eq. (2.9) that if the value of the thermal conductivity of a substance is high, it means that in this substances, the flow of heat per unit area per unit temperature gradient is high. Such substances are known as **thermal conductors**, and those for which the value of K is small are called **thermal insulators**. The unit of K is $\text{W m}^{-1} \text{K}^{-1}$. The thermal conductivity of metals like copper and aluminium is $400 \text{ W m}^{-1} \text{K}^{-1}$, and $240 \text{ W m}^{-1} \text{K}^{-1}$ respectively. On the other hand, the thermal conductivity of water is $0.6 \text{ W m}^{-1} \text{K}^{-1}$ and that of air is $0.02 \text{ W m}^{-1} \text{K}^{-1}$. To fix your ideas about thermal conductivity, you should solve an SAQ.

SAQ 4



An electric heater operating at 200 W is placed in a cubical box of insulating material. The length of a side of the box is 20 cm and the thickness of each side is 1 cm. After the heater has been on for a sufficiently long time, steady-state is achieved : the interior surfaces of the box remain at the temperature of 60°C while the exterior surfaces are at the temperature of 20°C.

- (a) Calculate the rate of flow of thermal energy out of the box.
- (b) Calculate the thermal conductivity of the material of the box.

2.4.2 Convection

Convection is another mechanism of heat transfer and it is characterised by the fact that **heat transfer takes place by physical movement of material particles from a region at higher temperature to a region at lower temperature**. Therefore, heat transport through this mechanism is observed in fluids. For example, in a hot air blower, air is heated by a heating element and is blown by a fan. The air particles carry the heat wherever it goes.

2.4.3 Radiation

You might have noted that, for transfer of heat through the processes of conduction and convection, presence of material medium is necessary. *However, we know that heat can be transferred in vacuum also.* You may ask : **How does it happen?** The mechanism through which heat transfer takes place in such situations is called **radiation**.

It is important to mention here that the term *radiation* is also used for electromagnetic waves. So, heat transfer through radiation process implies the heat energy is carried by electromagnetic waves. *Heat energy emitted by a material body on account of its temperature is known as thermal radiation.* The emitting body may be a source of energy itself, such as the sun or there may be a constant supply of energy to the body from the outside as in the case of the filament of an electric bulb. Thermal radiation belongs to infrared region of the electromagnetic spectrum. Therefore, they are also called **infrared radiation**.

You may be aware that, like any other wave, electromagnetic waves or radiations are characterised by its wavelength and frequency. A body at non-zero temperature emits radiation at all wavelengths. *However, the amount of energy radiated at a particular wavelength is a function of temperature.* For example, a body at very high temperature ($\sim 800^\circ\text{C}$) looks red because it emits radiations having larger wavelengths which fall in the red region of the visible portion of the electromagnetic spectrum. To elaborate these ideas further, let us learn some concepts such as emissive power and absorptance of materials.

Emissive Power

Emissive power (e_λ) of a body at a given temperature is defined as the total amount of heat energy emitted per unit time per unit area of the body in the form of radiation at all possible wavelengths. The unit of e_λ is $\text{J s}^{-1} \text{m}^{-2}$ or Wm^{-2} . It is also known as **emittance**. Emittance for tungsten at 2177°C is 500 kW m^{-2} .

Absorptance

Absorptance of a body *for a given wavelength* is defined as the ratio of the amount of radiation absorbed in a given time to the total radiation (heat), in the unit wavelength interval around the wavelength, incident upon it in the same time. It is denoted by a_λ . At 2477°C , the absorptance of tungsten is approximately 0.25.

Emissivity (ϵ)

Emissivity of a body at a given temperature is defined as the ratio of the total emissive power of the body (e_λ) to the total emissive power of a perfectly black body (E_λ) at that temperature. Mathematically, it is written as :

$$\epsilon_\lambda = \frac{e_\lambda}{E_\lambda}$$

$$\text{or} \quad e_\lambda = \epsilon_\lambda E_\lambda \quad \dots (2.10)$$

The knowledge of above terms related to heat transfer by radiation enables us to discuss a few laws governing emission and absorption of radiation by matter. Let us learn them now.

Kirchhoff's Law

According to this law, for a given wavelength, the ratio of emissive power to the absorptance for all bodies is always a constant at any given temperature. This constant is equal to the emissive power of a perfectly black body corresponding to the same wavelength at the same temperature. The ratio depends on the wavelength and temperature only and is independent of the nature of the emitting/absorbing surface and other conditions. Thus, we can write the emissive power for wavelength λ of a perfectly black body as :

$$E_\lambda = \text{constant} = \frac{e_\lambda}{a_\lambda} \quad \dots (2.11)$$

Black Body

A black body is defined as an object which absorbs radiations of all wavelengths incident on it. Conversely, a black body is also called a **perfect radiator**. This implies that when a perfectly black body is heated to a suitably high temperature, it emits radiations of all wavelengths and these radiations are called **black body radiations**. *Thus, ideally, a perfect radiator is also a perfect absorber.* However, no material surface is a perfect radiator and the notion of black body is an *idealization*. But the concept of a black body is very helpful in analysing many situations involving emission and absorption of radiations. One such situation is to know the relation between emission of radiation by a body and its temperature and the relation is given in the form of stefan's law.

Stefan's Law

This law addresses the question : **How do we quantify the amount of heat transferred through radiation by a body at a given temperature to its surroundings?** The early experiments to find answer of this question were done by Tyndall. The findings of these experiments were summarised by Stefan in the form of a law. Subsequently, Boltzmann provided a theoretical

basis for this law. Therefore, the law is also known as **Stefan-Boltzmann law**. According to this law, the amount of heat energy radiated per second by unit area of a perfectly black body is directly proportional to the fourth power of the absolute temperature (T) of the body. Mathematically, it is written as :

$$E = \sigma T^4$$

where σ ($= 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$) is called the **Stefan constant**.

The present day understanding of heat energy is based on the motion of microscopic particles of the body. The theoretical basis for such understanding is given by the kinetic theory. This theory helps us address questions like : Can the thermal properties of matter be explained in terms of the motion of its constituent microscopic particles like atoms or molecules? You will now learn the kinetic theory of gases.

2.5 KINETIC THEORY OF GASES

Kinetic theory of gases was developed to understand the relation between measurable macroscopic parameters (such as temperature and pressure) of gases, liquids and solids and the kinetic properties of the microscopic particles such as atoms and molecules of these system.

Analysis of these systems comprising a large number of atoms or molecules is a complex affair. Therefore, the kinetic theory of gases make some simplifying assumptions which are listed below :

- An infinitesimal volume of a gas contains a *large number of molecules, N* .
- A gas comprises identical molecules which behave as *rigid and perfectly elastic spheres*.
- The *molecules are in a perpetual random motion*; the molecules move in all directions with equal probability and with a variety of speeds.
- The average *inter-molecular distance is large compared with molecular diameters*. Thus, the molecules are assumed to have a negligible volume in comparison to the volume of the container of the gas.
- The molecules are assumed to *exert no force on other molecules except when they collide with one another and with the wall of the container of the gas*.
- Between collisions, molecules move with *uniform rectilinear motion*.
- The portion of the wall with which a molecule collides is considered to be smooth and the *collision is assumed to be perfectly elastic*.
- The duration of any collision is assumed to be very small compared with the time between collisions.
- When there is no external field of force, the molecules are *distributed uniformly* throughout the container of the gas.

When these simplifying assumptions are applied on a gaseous system, its analysis becomes simpler. Now, consider a gas in a container. Even at ordinary temperature and pressure, the molecules of the gas will collide with the walls of

the container. That is, a transfer of momentum between gas molecules and the wall of the container takes place. As a result, the walls experience a continuous force or pressure. You may like to know how much pressure is exerted by an ideal gas on its container. This knowledge will help us understand the kinetic interpretation of temperature.

2.5.1 Pressure Exerted by an Ideal Gas

Suppose an ideal gas is kept in a cubical container of side L . Let mass of each molecule be m and there are n molecules per cubic meter. In general, the number of molecules is very large and they possess different velocities. In the absence of an external force applied on the system, the molecules will exhibit complete chaos and collide with the walls of the container (Figure 2.6(a)). Let us first consider a molecule with velocity v . We can resolve v into three mutually orthogonal components v_x , v_y and v_z parallel to the sides of the cube (Figure 2.6(b)). Thus, we can write :

$$v^2 = v_x^2 + v_y^2 + v_z^2 \quad \dots (2.12)$$

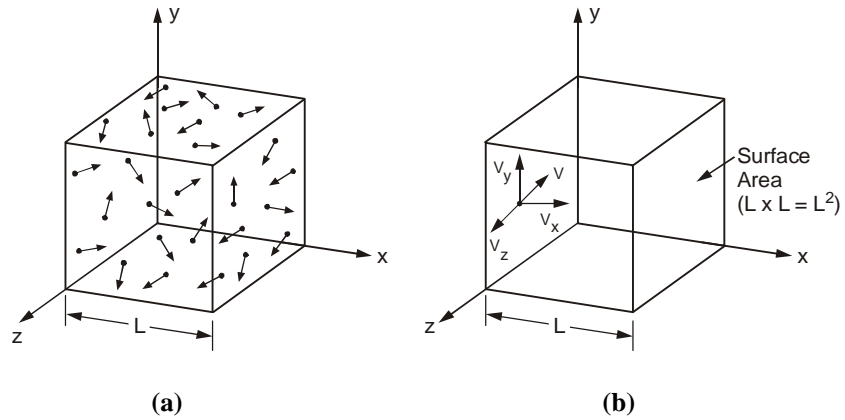


Figure 2.6 : (a) Velocity Vectors for the Molecules of a Gas in a Box; and (b) Mutually Orthogonal Components of Velocity v of a Molecule

Thus, the x -component of the momentum of the molecule will be mv_x normal to the face of the cube before collision. After it collides elastically with the wall of the container at $x = L$, its momentum in the opposite direction will be $-mv_x$. Therefore, in each collision, the change in x -component of the momentum of the molecule is,

$$\begin{aligned} \Delta p_x &= (p_x)_{\text{after collision}} - (p_x)_{\text{before collision}} \\ &= -m v_x - m v_x \\ &= -2m v_x \end{aligned}$$

An equal and opposite momentum will be transferred to the wall of the container. That is, in each collision, the value of the momentum transferred to the wall at $x = L$ is $2mv_x$.

Further, this molecule will have to travel across the cube and back, i.e. a distance of $2L$, to again strike the particular wall at $x = L$. Therefore, the time interval between two successive collisions of the molecule with a particular wall of the container will be $\Delta t = \frac{2L}{v_x}$.

Now, according to Newton's second law, the force (the rate of change of momentum) exerted by the molecule on the wall of the container can be written as :

$$\begin{aligned}
 f_x &= \frac{\Delta p_x}{\Delta t} \\
 &= \frac{2mv_x}{\left(\frac{2L}{v_x}\right)} \\
 &= \frac{mv_x^2}{L} \quad \dots (2.13)
 \end{aligned}$$

The force exerted by all the molecules can be written as summation of f_x over all molecules; that is :

$$\begin{aligned}
 F_x &= \sum_{[\text{all molecules (am)}]} f_x \\
 &= \sum_{am} \frac{mv_x^2}{L}
 \end{aligned}$$

Now, pressure is defined as the force per unit area. Thus, the pressure exerted by the molecules on a surface area L^2 of the wall at $x = L$ is

$$\begin{aligned}
 P &= \frac{F_x}{L^2} \\
 &= \sum_{am} \frac{mv_x^2}{L^3} \quad \dots (2.14)
 \end{aligned}$$

Since $L^3 = V$, the volume of the cube, we can write Eq. (2.14) as :

$$PV = \sum_{am} m v_x^2 \quad \dots (2.15)$$

The pressure of the gas is independent of the direction. Therefore, we can write the pressure of gas molecules on the walls perpendicular to y - and z -axes as :

$$PV = \sum_{am} m v_y^2 \quad \dots (2.16)$$

and

$$PV = \sum_{am} m v_z^2 \quad \dots (2.17)$$

From Eqs. (2.15), (2.16) and (2.17), we can write

$$3PV = \sum_{am} m (v_x^2 + v_y^2 + v_z^2)$$

Substituting Eq. (2.12), we get :

$$PV = \frac{1}{3} \sum_{am} m v^2 \quad \dots (2.18)$$

Further, the kinetic energy of all the molecules can be written as :

$$(\text{KE})_{\text{total}} = \sum_{am} \frac{1}{2} m v^2 \quad \dots (2.19)$$

Thus, from Eqs. (2.18) and (2.19), we can write :

$$PV = \frac{2}{3} (\text{KE})_{\text{total}} \quad \dots (2.20)$$

Kinetic Interpretation of Temperature

You may ask : **Why did we derive the expression for the pressure exerted by the gas molecules on the walls of the container?** It was done to relate the theoretical predictions with experimental observations. You know from basic thermal physics that the experimentally observed relation between pressure, volume and temperature of a gaseous system is given by the so called **equation of state** :

$$PV = N k_B T \quad \dots (2.21)$$

where N is the number of molecules in the gaseous system, T is its temperature and k_B is the *Boltzmann constant*. Comparing Eqs. (2.20) and (2.21), we get :

$$\begin{aligned} \frac{2}{3} (\text{KE})_{\text{total}} &= N k_B T \\ \text{or, } \frac{(\text{KE})_{\text{total}}}{N} &= \frac{3}{2} k_B T \quad \dots (2.22) \end{aligned}$$

Since N is the total number of molecules, we can write the average kinetic energy per molecule of the gas as :

$$\langle \text{KE} \rangle = \frac{(\text{KE})_{\text{total}}}{N} \quad \dots (2.23)$$

From Eqs. (2.22) and (2.23), we get :

$$\langle \text{KE} \rangle = \frac{3}{2} k_B T \quad \dots (2.24)$$

Eq. (2.24) shows that *the average kinetic energy per molecule of an ideal gas is proportional to the absolute temperature of the gas*. Also note that, at absolute zero of temperature, the gas molecules will be devoid of all motion. **This is kinetic interpretation of absolute zero temperature.** These are a few significant inferences from the kinetic theory of gases. It is instructive to note that the average kinetic energy of a molecule is independent of pressure, volume or the type of the molecules. Thus, the mean kinetic energy of all molecules will be the same at a given temperature despite the differences in their mass.

Root Mean Square Speed

As the temperature increases, the average speed of the molecules increases. In fact, molecules of the gas move with different speeds – some with high speed and some with low value of speed. Therefore, we use a characteristic speed, called root mean square speed (v_{rms}) for the molecules of a gaseous system. To find an expression for v_{rms} , we can write Eq. (2.24) as :

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$$

$$\text{or, } \langle v^2 \rangle = \frac{3 k_B T}{m}$$

$$\text{or, } \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$$

$$\text{or, } v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} \quad \dots (2.25)$$

You know from your school physics that gases obey certain laws such as Boyle's law and Charles's law. These laws are based on experimentally observed behaviour of gas under different conditions. It is, therefore, logical to check whether or not the kinetic theory of gases is able to predict these laws. You will learn it now. But, how about solving an SAQ?

SAQ 5



- (a) For one gram molecule of hydrogen at STP, calculate

- (i) root mean square speed,
- (ii) mean kinetic energy.

Take the density of hydrogen at STP as 0.09 kg m^{-3} .

- (b) Calculate the average energy of an air molecule at a temperature of 300 K.

2.5.2 Gas Laws from the Kinetic Theory

Boyle's Law

According to the Boyle's law, *the pressure of a given mass of a gas varies inversely with its volume, provided temperature remains constant.*

Mathematically, it is written as :

$$PV = \text{constant}$$

Now, from Eq. (2.20), we note that :

$$(\text{KE})_{\text{total}} = \frac{3}{2} PV$$

Since the kinetic energy will remain constant at a given temperature, above equation implies that :

$$PV = \text{Constant}$$

Charles' Law

According to this law, *if the pressure is kept constant, the volume of a gas increases linearly with the absolute temperature.* That is :

$$\frac{V}{T} = \text{Constant}$$

Now, again from Eq. (2.20) we note that, at a constant pressure, volume, V of the gas is linear function of the kinetic energy. This implies that the volume of the gas is a linear function of temperature, T (as kinetic energy is a linear function of T (Eq. 2.24)).

Avogadro's Law

This law states that, *at constant temperature and pressure, equal volumes of all gases contain the same number of molecules*. To derive this law from the kinetic theory, let us consider equal volumes V_1 and V_2 of two different gases at the same temperature and pressure. Let there are n_1 and n_2 molecules respectively in the equal volumes of the two gases. Thus, from Eq. (2.18), we can write :

$$\frac{1}{3} n_1 m_1 \langle v_1^2 \rangle = \frac{1}{3} n_2 m_2 \langle v_2^2 \rangle \quad \dots (2.26)$$

(because $PV = \text{Constant}$ as per the Boyle's law)

In Eq. (2.26), $\langle v_1^2 \rangle$ and $\langle v_2^2 \rangle$ respectively denote the mean squared speeds of the molecules of the two gases.

Further, at the same temperature, the mean kinetic energies of the two gases will be equal (Eq. (2.24)). Thus, we can write :

$$\frac{1}{2} m_1 \langle v_1^2 \rangle = \frac{1}{2} m_2 \langle v_2^2 \rangle \quad \dots (2.27)$$

From Eqs. (2.26) and (2.27), we get

$$n_1 = n_2 \quad \dots (2.28)$$

Eq. (2.28) is the Avogadro's law.

Now let us summarise what you have learnt in this unit.

2.6 SUMMARY

- Heat is a form of energy which is transferred from one object to another due to the temperature difference between the two objects. The practical unit of heat energy is calorie.

$$1 \text{ calorie} = 4.186 \text{ Joule}$$

- Temperature is a physical parameter of a body which quantifies our subjective sense of hot and cold. The relation between the Celsius and Fahrenheit scales of temperature is :

$$F = \left(\frac{9}{5} C \right) + 32$$

- According to the Zeroth law of thermodynamics, if two bodies are separately in thermal equilibrium with a third body, then the two bodies are also in thermal equilibrium with each other. This law helps us to measure temperature.
- The specific heat capacity of a substance is defined as the amount of heat required to raise the temperature of unit mass of the substance by unit degree. Mathematically, it is written as :

$$c = \frac{1}{m} \left(\frac{Q}{\Delta T} \right)$$

- Joule's mechanical equivalent of heat (J) is defined as the amount of work done (W) to produce a unit quantity of heat. Mathematical expression for J is :

$$J = \frac{W}{Q}$$

- The thermal conductivity (K) of a substance is given by

$$K = - \frac{\left(\frac{dQ}{dt} \right)}{A \left(\frac{dT}{dx} \right)}$$

where $\frac{dQ}{dt}$ is the rate of heat flow, $\frac{dT}{dx}$ is the temperature gradient and A is the area of cross-section of the material specimen.

- Kirchhoff's law states that the ratio of emissive power (e_λ) to the absorptive power (a_λ) corresponding to a particular wavelength λ and at any given temperature is always a constant for all bodies. This constant is equal to the emissive power (E_λ) of a perfectly black body at the same temperature and corresponding to the same wavelength. That is,

$$\frac{e_\lambda}{a_\lambda} = \text{constant} = E_\lambda$$

- A perfectly black body is one which absorbs radiations of all wavelength incident on it.
- Stefan-Boltzmann law states that the amount of heat energy (E) radiated per second by unit area of a perfectly black body is directly proportional to the fourth power of absolute temperature (T) of the body. The expression is :

$$E = \sigma T^4$$

where σ is the Stefan-Boltzmann constant. Its value is $5.6703 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.

2.7 ANSWERS TO SAQs

SAQ 1

Let x is the numerical value which is the same on the Celsius and Fahrenheit scales. Therefore, from Eq. (2.1), we can write :

$$x = \left(\frac{9}{5} x \right) + 32$$

or, $9x = 5x - 160$

or, $x = -40$

So the desired values are -40°F and -40°C .

SAQ 2

- (a) From the definition of the specific heat capacity and the calorimetric relation, we can write :

Heat gained by copper = Heat lost by water

$$c_{\text{copper}} m_{\text{copper}} \Delta T_{\text{increase}} = c_{\text{water}} m_{\text{water}} \Delta T_{\text{decrease}}$$

$$c_{\text{copper}} \times (250 \text{ g}) \times (26.8 - 20)^\circ\text{C} = 1 \text{ cal g}^{-1} \text{ K}^{-1} \times 50 \text{ g} \times (30 - 26.8)^\circ\text{C}$$

where we have taken $c_{\text{water}} = 1 \text{ cal g}^{-1} \text{ K}^{-1}$. Thus,

$$c_{\text{copper}} = 0.094 \text{ cal.g}^{-1}.\text{K}^{-1}$$

The heat capacity, C of the copper calorimeter is given by the product of its mass and the specific heat of copper :

$$\begin{aligned} C &= (250 \text{ g}) \times (0.094 \text{ cal g}^{-1} \text{ K}^{-1}) \\ &= 23.5 \text{ cal K}^{-1} \end{aligned}$$

- (b) The calorimetric relation suggests that heat lost by the aluminium block is equal to the heat gained by the copper calorimeter and the water in it :

$$\begin{aligned} (300 \text{ g}) \times c_{\text{aluminium}} \times (100 - 30.4) &= (250 \text{ g}) \times (0.094 \text{ cal.g}^{-1} \text{ K}^{-1}) \\ &+ 400 \text{ (g)} \times 1 \text{ cal.g}^{-1} \text{ K}^{-1} (30.4 - 20) \text{ C} \end{aligned}$$

$$\text{or, } c_{\text{aluminium}} = 0.211 \text{ cal g}^{-1}.\text{K}^{-1}$$

SAQ 3

As given in the problem, $h = 40 \text{ m} = 4000 \text{ cm}$; $M = 5 \text{ kg} = 5000 \text{ g}$; and $g = 980 \text{ cm s}^{-2}$.

From Eq. (2.8), we have

$$\begin{aligned} Q &= \frac{W}{J} \\ &= \frac{m g h}{J} \\ &= \frac{4000 \text{ (cm)} \times 5000 \text{ (g)} \times 980 \text{ (cm s}^{-2}\text{)}}{4.2 \times 10^7 \text{ (erg. cal}^{-1}\text{)}} \\ &= 466.7 \text{ cal} \end{aligned}$$

And, according to the calorimetric relation :

$$Q = m c \Delta T$$

where ΔT is the increase in temperature of water. We have from the problem, $m = 0.5 \text{ kg} = 500 \text{ g}$. Thus,

$$\begin{aligned} 466.7 \text{ cal} &= (500 \text{ g}) \times (1 \text{ cal.g}^{-1} \text{ K}^{-1} \times \Delta T \\ \Delta T &= 0.93 \text{ K.} \end{aligned}$$

SAQ 4

- (a) In the steady-state, the thermal energy from the electric heater passing into the walls of the box must be equal to thermal energy leaving the box. Thus, we can write :

$$\begin{aligned} \frac{dQ}{dt} &= 200 \text{ W} \\ &= 200 \text{ J s}^{-1} \\ &= \frac{200}{4.19} \text{ cal.s}^{-1} \end{aligned}$$

$$= \frac{200}{4.19 \times 10^3} \text{ kcal.s}^{-1}$$

$$= 0.048 \text{ kcal s}^{-1}$$

- (b) The total area A of the cube can be taken as the area of one side, $0.2 \text{ m} \times 0.2 \text{ m}$, multiplied by the number of sides (6) of the cube. The thickness L of each wall of the cube is 0.01 m . Since the edge length of the side of the cube is larger than its thickness, we may neglect the heat flow along the cube edges. Thus, from Eq. (2.9);

$$\begin{aligned} K &= \frac{\left(\frac{dQ}{dt} \right)}{A \left(\frac{dT}{dx} \right)} \\ &= \frac{(0.048 \text{ kcal s}^{-1}) \times (0.01 \text{ m})}{6 \times (0.2 \text{ m}) \times 0.2 \text{ m} \times (60 - 20) \text{ }^\circ\text{C}} \\ &= 5.0 \times 10^{-5} \text{ kcal m}^{-1} \text{ s}^{-1} \text{ }^\circ\text{C}^{-1} \end{aligned}$$

Good thermal insulators, such as asbestos, have thermal conductivities of this order.

SAQ 5

- (a) (i) Using Eq. (2.21) and (2.25), we can write :

$$\begin{aligned} P &= \frac{1}{3} \frac{m N v_{\text{rms}}^2}{V} \\ &= \frac{1}{3} \frac{M}{V} v_{\text{rms}}^2 \end{aligned}$$

where $m \times N = M$, the molecular weight. Further, for 1 gram molecule of hydrogen,

$$\begin{aligned} \text{Density } (\rho) &= \frac{\text{Mass}}{\text{Volume}} \\ &= \frac{M}{V} \end{aligned}$$

Substituting for $\frac{M}{V}$ in the above relation, we get :

$$P = \frac{1}{3} \rho v_{\text{rms}}^2$$

We have $\rho = 0.09 \text{ kg m}^{-3}$

and at S. T. P., Pressure $P = 1.01 \times 10^5 \text{ Pa}$. Substituting these values, in the above relation, we get

$$\begin{aligned} v_{\text{rms}} &= \sqrt{\frac{3 \times (1.01 \times 10^5 \text{ Pa})}{0.09 \text{ kg m}^{-3}}} \\ &= 1836 \text{ ms}^{-1} \end{aligned}$$

- (ii) We know that the volume occupied by one mole of hydrogen at S. T. P. is,

$$V = 22.4 \text{ litres}$$

$$= 22.4 \times 10^{-3} \text{ m}^{-3}$$

Further, $\text{Density} = \frac{\text{Mass}}{\text{Volume}}$

or, $\text{Mass} = \text{Density} \times \text{Volume of hydrogen,}$

$$M = (0.09 \text{ kg m}^{-3}) \times (22.4 \times 10^{-3} \text{ m}^{-3})$$

$$= 2.016 \times 10^{-3} \text{ kg}$$

We can write :

$$\text{The average kinetic energy per mole} = \frac{1}{2} M v_{rms}^2$$

$$= \frac{1}{2} \times (2.016 \times 10^{-3} \text{ kg}) \times (1836 \text{ ms}^{-1})^2$$

$$= 3397.8 \text{ J}$$

- (b) From Eq. (2.24), we have the average kinetic energy per molecule is given by

$$\langle KE \rangle = \frac{3}{2} k_B T$$

$$= \frac{3}{2} \times (1.38 \times 10^{-23} \times \text{JK}^{-1}) \times (300 \text{ K})$$

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