## HEAT

# 11.1. Heat as a form of energy in Transit.

Many scientists have tried to explain the nature of heat. Up to the beginning of the nineteenth century, it was considered a weightless fluid called caloric which existed in every material body. Hot bodies were said to contain more caloric than the cold bodies. The caloric theory could explain satisfactorily many processes such as heat conduction and mixing of substances in a calorimeter.

This concept of heat fluid was challenged by Count Rumford. He observed while supervising the boring of cannon that as cannon barrels were being bored, a tremendous amount of heat was given off. According to the caloric theory since the metal chips cut off by the drill have lost caloric i.e the heat given off in the drilling process, the chips should not be the same as the original metal, which had not lost caloric. But Rumford was unable to find any difference between the chips and the original metal in respect to their ability to hold or give off heat. In order to further investigate it, Rumford made use of a very dull drill, which was unable to cut the metal. Heat was evolved in apparently unlimited quantity as long as the borer was rotated and the supply of heat was inexhaustible. He concluded that heat was due to the rotation of the borer and not from the metal itself.

As a result of this experiment and experiment performed by Joule, the scientists came to interpret heat not as the flow of substance(caloric) but as transfer of energy when heat flows from a hot body to a cold one. It is energy that is being transferred from the hot to the

S.

cold object. Thus heat refers to energy that is transferred from one body to another because of difference in temperature. Heat is not the energy that a body contains in it. It refers to the amount of energy transferred from hot to a cold body. Once the heat energy is transferred to a body, it is converted in to the internal energy of the body. The internal energy is the sum of all the microscopic kinetic and potential energies of the molecules in the body. The S.I unit of heat, as for any form of energy is joule.

### 11.2. Temperature

If we take two bodies, we can say by the sense of touch whether one is hotter than the other. It is not possible to determine, how much hotter it is at a particular time than the other. We find that it is not possible to determine the degree of hotness by sense of touch. The quantitative determination of the degree of hotness may be termed as temperature. Before describing the measurement of temperature it is appropriate here to define thermal equilibrium, when two bodies at different temperatures are brought in thermal contact with each other. The heat starts flowing from the hot body to the cold body till the temperature of the bodies becomes same, then they are said to be in thermal equilibrium.

## 11.3. Scales of temperature

a body accurately by simply sense of touch or by comparing the degree of hotness. So a temperature scale is needed to measure the temperature quantitatively. For this we must have two reference points that are fixed and easily reproduceable. That is, the value of the fixed points must always be the same under similar conditions. The scale depends upon these fixed points.

The melting point of ice and boiling point of water

at standard pressure (76 cm of Hg) are taken to be the two fixed points and difference between these two points is divided in different ways called scales of graduation (Celsius and Fahrenheit, etc.).

On the Celsius (Centigrade) scale this interval between these fixed point is divided into hundred equal parts. The lower fixed point is marked 0 and upper fixed point 100. Each part thus represents one degree Celsius (1°c). This scale was suggested by Celsius in 1742.

On the Fahrenheit scale the lower fixed point is marked 32 and the upper fixed point 212, and the interval between them is equally divided into 180 equal parts. Each part represents one degree Fahrenheit (1°F).

There is an other scale called the Kelvin scale.

The lowest temperature on this scale is-273°c. Thus the zero on the Celsius scale will be 273 on the Kelvin scale written as 273K and 100 on Celsius scale will be 373K. The size of the degree on the Kelvin scale is the same as that of Celsius scale.

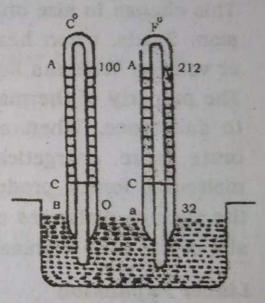


Fig: (11.1)

In order to derive relationship between centigrade and Fahrenheit scales let the two thermometers be placed in a bath and the mercury in each thermometer rises to the same level Fig. 11.1.

We arrive at the relation:

$$\frac{CB}{AB} = \frac{F - 32}{212 - 32} = \frac{C - 0}{100}$$

$$= \frac{F - 32}{180} = \frac{C}{100}$$

$$= \frac{F - 32}{9} = \frac{C}{5} - - - - - (11.1)$$

## 11.4. Thermometric Properties

Property of a substance which changes uniformly with the change of temperature is named thermometric property. For example the volume of a liquid in a vessel, the volume of a fixed mass of gas kept at constant pressure, the pressure of a fixed mass of gas maintained at constant volume, electrical resistance of a metal are some of the many measurable physical properties which changes with the change of temperature.

## 11.5. Thermal Expansion

It is a matter of daily observation that in general bodies undergo change in size when they are heated. This change in size on heating is termed Thermal Expansion. Solids, when heated show increase in length, area or volume. Whereas liquids and gases expand in volume. The property of thermal expansion varies from substance to substance. When a solid is heated, its molecules vibrate more energetically against the action of intermolecular forces producing greater displacement. Since the average distances among the molecules increase, the size of the solid increases.

## Linear Expansion

Expansion in length of solids on heating is called linear expansion. The observed expansion in length depends upon the original length and the change in temperature.

It has been found experimentally that the change in length is directly proportional to the original length and the change in temperature of the solid.

Suppose L is the length of a uniform thin metallic rod at some initial temperature. When it is heated through a small temperature  $\Delta T$ , an increase of length  $\Delta L$ 

takes place. So we can put it as.

$$\Delta L = \alpha L \Delta T$$
 ----- (11.2)

where a is a constant of proportionality, which depends upon the material of rod and called the co-efficient of linear expansion.

Equation 11.2 can be rewritten as:

$$\alpha = \frac{\Delta L}{L\Delta T} - (11.3)$$

From Eq.11.3, the co-efficient of linear expansion  $\alpha$  is defined as the change in length per unit length per Kelvin rise in temperature. Its unit is K

If L' is the length of the rod after heating then,

hence equation 11.2 can be written as

$$L'-L = \alpha L\Delta T$$
or 
$$L' = L (1+\alpha \Delta T) ----- (11.4)$$

A list of the average values of common solids is given below in table 11.1.

Table 11.1

S. No.	Substance		(K <sup>-1</sup> )
1 2 3 4 5	Aluminium Brass and Bronze Copper Glass(ordinary) Glass(Pyrex)	24×10 <sup>-6</sup> 19×10 <sup>-6</sup> 17×10 <sup>-6</sup> 9×10 <sup>-6</sup> 3,2×10 <sup>-6</sup>	2.4×10 <sup>-5</sup> 1.9×10 <sup>-5</sup> 1.7×10 <sup>-5</sup> 0.9×10 <sup>-5</sup> 0.32×10 <sup>-5</sup> 8.0×10 <sup>-5</sup>
6 7 8 9 10	Hard Rubber Ice Invar (Ni-Cr.alloy) Lead Steel Concrete	80x10 <sup>-6</sup> 51x10 <sup>-6</sup> 0.9x10 <sup>-6</sup> 29x10 <sup>-6</sup> 11x10 <sup>-6</sup> 12x10 <sup>-6</sup>	5.1x10 <sup>-5</sup> 0.09x10 <sup>-5</sup> 2.9x10 <sup>-5</sup> 1.1x10 <sup>-5</sup> 1.2x10 <sup>-5</sup>

Example 11.1.

A steel rod has a length of 10m at a temperature of 25°C. What will be the increase in length if the temperature is raised to 35°C.? Given  $\alpha = 1.1 \times 10^{-5} \text{ K}^{-1}$ 

Solution

L = 10 m

AT = 35°C - 25°C = 10°C = 10K

from eq:11.2

Since  $\Delta L = L \alpha \Delta T$ .

 $= (10m)(1.1\times10^{-5} \text{ K}^{-1} \times 10\text{K})$ 

 $= 1.1 \times 10^{-3} \text{m}$ 

## 11.6. Volume Expansion

We discussed above expansion in one dimension only but as a matter of fact the solids expand on heating in all the three dimensions i.e.length, breadth and thickness.

Consider a metallic body of volume V at some initial temperature. Its volume changes by  $\Delta V$  when temperature changes by  $\Delta T$ . It is found experimentally that

 $\Delta V \propto V \Delta T$ 

or  $\Delta V = \beta V \Delta T - (11.5)$ 

where  $\beta$  is a constant of proportionality known as coefficient of volume expansion, its unit is also  $\bar{K}^1$ .

Let there be an object in the shape of a rectangular box of dimensions l,w and h. Its volume V at some initial temperature T is given by

V = lt. w

If the temperature changes to  $T + \Delta T$ , its volume changes to  $V + \Delta V$  where each linear dimension changes following

The terms containing  $(\Delta T)^2$  and  $(\Delta T)^3$  are negligibly small. Therefore the Eq. (11.6) reduces to

$$V + \Delta V = V + (3 \alpha) V \Delta T$$

$$\Delta V = (3 \alpha) V \Delta T - (11.7)$$

Comparing Eq. 11.5 and Eq. 11.7 we see that

Or

$$\beta = 3\alpha$$
 ----- (11.8)

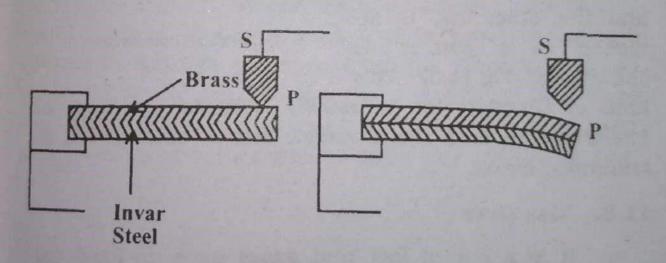


Fig: (11.2)

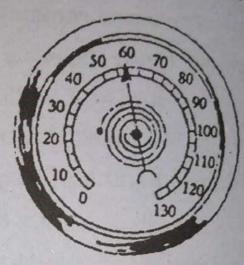
## 11.7. Bimetallic Thermostat

One of the examples of thermal expansion is of thermostat devices. Thermostats are well known devices commonly used for maintaining required temperatures. We describe below a common type of thermostat called bimetallic thermostat. The bimetallic strip works as an electric contact breaker in an electrical heating circuit. The circuit is broken when the desired temperature of the bath is reached. Due to the difference in the coeffi-

cients of linear expansion of the two metals, the metallic strip bends in the form of a curve and the circuit is broken. In Fig. 11.2 (a) the metallic strip is in contact with the screw S and in the Fig. 11.2 (b) the strip curves downwards as it becomes hot and contact at P is broken. Thus the current stops flowing through the heating coil. When the temperature falls, the strip contracts and the contact at P is restored. The two metal strips are very well joined.

#### Bimetallic Thermometer:

Similarly a bimetallic strip can be used to make a thermometer. In this case the bimetallic strip often is in the form of a coil. Its one end is fixed and the other end is attached to a pointer as shown in Fig.11.3. This



Bimetallic Thermometer Fig:(11.3)

kind of thermometer is usually used for ordinary air thermometer, oven thermometer, and in automobiles for automatic choke.

#### 11.8. Gas Laws

It is a known fact that gases have no fixed volume or shape and their volume can be altered by changing the pressure as well as the temperature. The behaviour of a gas can be described with the help of four variables i.e. pressure, volume, mass and temperature. The relation between any two variables is found experimentally while keeping the other constant.

## (1) Boyle's Law

Let us consider the relation between the pressure and volume of a given mass of gas at constant mass and temperature. It was found experimentally by Robert

Boyle in 1660 that for a fixed mass of a gas at constant temperature, the product of pressure (P) Volume (V) is constant. This is known as Boyle's Law. In symbols we can write as:

P V = a constant (temp: remaining constant) 11.9.

#### Charles's Law (2)

When a given mass of a gas is heated at constant pressure experiments show that the volume V of a given mass of a gas is directly proportional to its absolute temperature T. In symbols, we can put as:

V/T =a constant (pressure remaining constant)----(11.10) This law was investigated by Charles and is known as Charles's Law

On plotting a graph of volume of the gas against its temperature, a straight line is obtained. It shows that equal changes in temperature lead to equal changes in volume at constant pressure. From the graph it is found that at 0°C the gas still possesses a volume Vo. When the straight line of the graph is extrapolated to lower and lower temperature axis as shown by the dotted line,

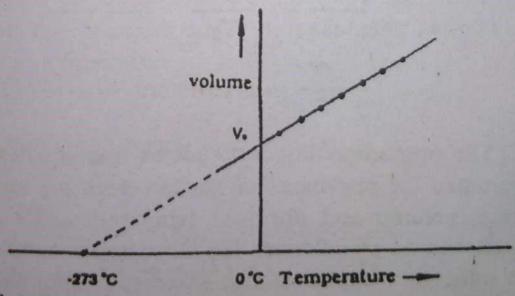


Fig:(11.4)

it intersects the temperature axis at a temperature of -273°C. This implies that if a gas could be cooled to -273°C. It would have no volume. - 273°C is called the

absolute zero of the temperature.

#### 11.9. General Gas Law

In order to derive general gas law we make use of both these gas laws. Let P<sub>1</sub>,V<sub>1</sub> and T<sub>2</sub> be the pressure volume and absolute temperature of a given sample of a gas of mass m.

According to Boyle's Law, the change in pressure from P<sub>2</sub> to P<sub>1</sub> is accompained by a change in volume from V<sub>1</sub> to V. This can be expressed mathematically

$$P_1 V_1 = P_2 V$$

$$V = \frac{P_1 V_1}{P_2} - \dots - (11.11)$$

Now by changing the temperature from T<sub>1</sub> to T<sub>2</sub> at constant pressure P<sub>2</sub> the volume of the gas changes from V to V<sub>2</sub>, then according to Charles's Law we have

$$\frac{V}{T_1} = \frac{V_2}{T_2}$$
 ---- (11.12)

Using Equation 11.11 in Equation 11.12, we get

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad (11.13)$$

or 
$$\frac{PV}{T}$$
 = a constant ----- (11.14)

The proportionality constant in this equation can be evaluated for any mass of gas provided we know its pressure, volume and absolute temperature. Its value, however, has no significance for other given samples because different samples of the same gas differ in mass and hence in number of molecules. It is convenient to express the amount of gas in a given volume in terms of the number of moles, n.

By definition, a mole of any substance is that

mass of the substance that contains a specific number of molecules called Avogadro's number, NA. The value of N, is approximately 6.022 x1023 molecules/mole. Avogadro's number is defined to be the number of carbon atoms in 12g of the isotope carbon12. The number of moles of a substance is related to its mass m. through the expression

$$n = m/M$$

where M is a quantity called the molecular weight of the substance, usually expressed in g/mole.

In such cases Eq.11.14 may be written as

Where R is called the universal gas constant and does not depends on the quantity of gas in the sample. If P is measured in N m<sup>-2</sup>, V in m<sup>3</sup> and T in Kelvin then the value of Universal gas constant is

#### Example 11.2.

An air-storage tank whose volume is 112 liters contains. 3kg of air at a pressure of 18 atmospheres. How much air would have to be forced into the tank to increase the pressure to 21 atmospheres assuming no change in temperature.

#### Solution

Here 
$$P_1 = 18$$
 atm  $P_2 = 21$  atm  $V_1 = 112$  liters  $V_2 = V_1$   $m_1 = 3$  kg  $m_2 = ?$   $\frac{P_1 V_1}{m_1} = \frac{P_2 V_2}{m_2}$   $\frac{P_2 V_2}{m_2}$   $\frac{18 \times 112}{3} = \frac{21 \times 112}{m_2}$  or  $m_2 = 3.5$  kg.

OL

The mass of air which must be forced into the tank is (3.50-3.00) = 0.5 kg.

### Example 11.3.

Calculate the volume occupied by a gram-mole of a gas at 0°C and a pressure of 1 atmosphere.

Solution

P = 1 atm = 1.01 x 10<sup>5</sup> Nm<sup>-2</sup>  
T = 0°C + 273 = 273 K  
n = 1  
R = 8.314 J/mole.K.  
PV = n R T  
1.01 x 10<sup>5</sup> V = 1 x 8.31 x 273  
V = 
$$\frac{1 \times 8.314 \times 273}{1.01 \times 10^5}$$

- $= 0.0224 \text{ m}^3/\text{mole}$
- = 22.4 liters/mole as  $1m^3 = 1 \times 10^3$  liters.

# 11.10. The Properties of Gases; Kinetic Interpretation

The properties of matter in bulk can however be predicted on molecular basis by a theory known as kinetic theory. The first step in the construction of a theory is to set up some sort of model which is simple enough to be treated mathematically. The characteristics of the model are described by a set of fundamental assumptions which for the kinetic theory of gases are:

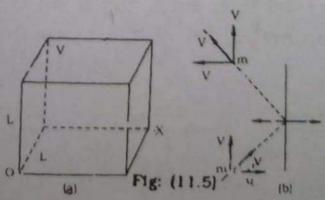
- 1. A gas consists of particles called molecules. Depending on the gas each molecule will consist of an atom or a group of atoms. All the molecules of a gas in a stable state are considered identical.
- 2. Any finite volume of a gas consists of very large number of these molecules. This assumption is

justified by experiments. At standard conditions there are 3x 1026 molecules in a cubic metre.

- The molecules are separated by distance large as 3. compared to their own dimensions. The diameter of a molecule, considered as a sphere, is about 3 x 10
- The molecules move in all directions and with various speeds making elastic collisions with one another and with the walls of the container. The walls of a container can be considered perfectly smooth.
- Molecules exert no forces on one another except 5. during collisions. Therefore in between collisions with other molecules or with the walls of the container, and in the absence of the external forces, they move freely in straight lines.
- Newtonian mechanics is applicable to the motion 6. of molecules.

# 11.11. Interpretation of Pressure on Kinetic theory of Gases

In order to calculate the pressure of an ideal gas from kinetic theory. Let us consider (i) N number of molecules contained in a cubical vessel whose walls are perfectly elastic (ii) the faces of the cube which are normal to the x-axis and having edge length L. Figure 11.5 (a). (III) A molecule which has a velocity v can be resolved into components vx,vy,vz in the direction of the edges.



If we have a molecule which collides with one face A of the cube, it will rebound such that x-component of the velocity  $v_x$  is reversed, the  $v_y$  and  $v_z$  remain unaffected ed Fig (11.5 (b).) Therefore the momentum before collision is  $mv_x$  and after collision - $mv_x$  causing a change of momentum (momentum after collision - momentum before collision).

$$mv_x - (-mv_x) = 2mv_x$$
 ----- (11.16)

normal to the face A. Hence the momentum given to the face A will be  $2mv_x$ , since the total momentum is conserved. The time required by the molecule to reach from one face to the other without collision will be  $1/v_x$ . The round trip will be covered in time  $t = 2\ell/v_x$ . The number of collisions per second against the face A would then be

$$\frac{1}{t} = \frac{1}{2\ell/v_x} = v_x/2\ell$$

Therefore the rate at which the molecule transfers its momentum to face A is found by multiplying the number of collision the molecule suffers at the face A, and the momentum it transferred to the face of each collision.

$$2mv_x - \frac{v_x}{2\ell} = \frac{mv_x^2}{\ell}$$
 (11.17)

Relation (11.17) is rate of change of momentum of the molecule on striking the face A of the cube i.e. the molecule is exerting a force  $mv_x^2/\ell$  on striking the face A. To obtain the total force on A due to all the gas molecules, we sum up  $mv_x^2/\ell$  for all the molecules and so it will be

$$\frac{mv_{1x}^{2}}{\ell} + \frac{mv_{2x}^{2}}{\ell} + \frac{mv_{3x}^{2}}{\ell} + \cdots + \frac{mv_{nx}^{2}}{\ell}$$

where  $v_{1x}$  is the x-component of the velocity of 1st particle  $v_{2x}$  is that of 2nd particle ........ and  $v_{nx}$  is that of nth particle. As m is the mass of one molecule then to find the pressure p, divide this force by the area of the face A, namely  $\ell^2$ , so

$$P = (m/\ell^3) (v_{1x}^2 + v_{2x}^2 + ..... + v_{nx}^2) ---- (11.18)$$

The number of molecules in unit volume  $n_v$  is  $\frac{N}{\ell^3}$  where N is the total number of molecules, therefore

13=N/n, and substituting this value in equation (11.18), we have

$$P = mn_v (v_{1x}^2 + v_{2x}^2 + .....)/N$$
 -----(11.19)

where mn is the mass per unit volume which we call density  $\rho \left(v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots \cdot v_{nx}^2\right)/N$  is the aver-

age value of  $v_x^2$  for all the particles in the container we call this average square velocity ( $v_x^2$ ). The Square root of  $v_x^2$  is referred as  $V_{rms}$ . Eq. 11.19 can be written as

$$P = \rho v^{2}$$
 (11.20)

The term  $v_x^2$  is only one component of the total velocity, since  $v^2 = v_x^2 + v_y^2 + v_z^2$ . On the average.

 $v_x^2 = v_y^2 = v_z^2$ , due to the randomness of the molecular motions,  $v^2 = 3v_x^2$  and  $v_x^2 = \frac{1}{3}v^2$ . Substituting this value into the equation above, we find that

$$P = \frac{1}{3} \rho \sqrt{2}$$
 (11.21)

Example 11.4.

O.00°C and 1.00 atm pressure, assuming hydrogen to be

an ideal gas. Under these conditions hydrogen has a density  $\rho$  of 8.99 x 10<sup>2</sup> kg/m<sup>3</sup>.

Solution

Since 
$$p = 1.00 \text{ atm} = 1.01 \times 10^5 \text{ Nm}^{-2}$$

so using  $v_{rms} = \sqrt{3p/\rho}$ , and substituting the values of  $\rho$  and P we have

$$v_{\text{rms}} = \sqrt{\frac{3 \times 1.01 \times 10^5 \,\text{Nm}^{-2}}{8.99 \times 10^{-2} \,\text{kg m}^3}}$$

$$= 1835.86 \text{ ms}^{-1}$$

This is of the order of nearly two km per second.

#### 11.12. Derivation of the Gas Laws

The gas laws can be derived using Eq 11.21

$$P = \frac{1}{3} \rho v^{2}$$
  
=  $\frac{1}{3} n_{v} m v^{2}$  (since  $\rho = mn_{v}$ ) -----(11.22)

Since n<sub>v</sub> represents the number of molecules per unit volume N/V, we can write the Eq. (11.22) as

$$p = \frac{1}{3} \frac{N}{V} \text{ m } \frac{\sqrt{2}}{V^2}$$

$$PV = \frac{1}{3} \text{ Nm } \sqrt{2} \qquad -----(11.23)$$

Comparing it with Eq (11.15) we find that

$$\frac{1}{3}$$
 Nm  $v^2 = n R T$ . -----(11.24)

Substituting  $n = N/N_A$  and multiplying both sides by 3/2, we obtain the relation

$$1/2 \text{ m } v^2 = (3/2) (R/N_A)T$$

Since  $R/N_A = k$  (Boltzmann constant) = 1.38 x10<sup>-23</sup> J/ (molecule - K)

Hence 
$$\frac{1}{2}$$
 m  $v^2$  = (3/2) k T. ----(11.25)

This equation indicates that the average translational kinetic energy per molecule is directly proportional to the absolute temperature and it could serve to define temperature in terms of mechanical quantities.

Thus Eq.11.23 shows that if v<sup>2</sup> remains constant, the temperature remains constant which is the condition for Boyle's Law.

From Eq 11.23 and 11.25, we have

$$V = \frac{N}{P} kT$$
 ----- (11.25)

If  $\rho$  is constant, the factor  $\frac{Nk}{P}$  is a constant, thus  $V \propto T$ , which is Charles's Law.

## 11.13. Specific Heat Capacity

It is found experimentally that one kilogram of copper requires considerably less amount of heat to raise its temperature by 1°C than one kilogram of water. Likewise one kilogram of paraffin requires about half as much heat to raise its temperature by 1°C as does one kilogram of water. These examples demonstrate that equal amounts of different substances absorb different amount of heat when heated to the same temperature.

The examples discussed above introduce the idea of specific heat of a substance which is defined as the amount of heat required to raise the temperature of unit mass of the substance to unit degree rise of temperature. If a body of mass is heated so that its temperature rises from T to  $T + \Delta T$  and it absorbs a small amount of heat  $\Delta Q$ , then its heat capacity C is defined as

$$C = \frac{\Delta Q}{\Delta T} \qquad (11.27)$$

whereas specific heat capacity  $c = \frac{C}{mass} = \frac{\Delta Q}{m\Delta T}$  at temperature T.

The value of specific heat of water is 4200 J kg<sup>-1</sup>(K)<sup>-1</sup>. Specific Heat is a characteristic of the material of which the substance is made of. The values of specific heat of different materials are given in the table 11.2.

TABLE 11.2.

Sr.	Substance	Specific Heat	
No:		J kg-1 K-1	
1.	Aluminium	903.00	
2.	Carbon	508.200	
3.	Copper	386.00	
4.	Iron	499.800	
5.	Lead	128.100	
6.	Mercury	138.600	
7.	Silver	230.00	
8.	Tungsten	134.800	
9.	Water	4180.00	
10.	Ice	2100.00	

## 11.14. Determination of the Specific Heat Capacity

The method described below is known as the method of mixtures and is regarded as the most fundamental method of determining the specific heat capacity of solids and liquids. This method is based on the principle; that heat lost by hot bodies is equal to that gained by the cold bodies:

Heat lost = Heat gained.

This is called the law of heat exchange.

The method of mixtures utilises the fact that when a hot substance is mixed with the cold one. the

hotter one loses heat and the cooler one absorbs heat until both finally attain the same temperature.

The specific heat of the substance of known mass and temperature is determined by mixing it with liquid of known mass and temperature in a vessel called calorimeter of known mass and temperature. The final temperature of the mixture is measured. The specific heat capacity of the substance can be calculated from the given data. The following example will further illustrate the method of mixtures for calculating the specific heat capacity of a substance.

### Example 11.5.

A 50 gram piece of metal is heated to 100°C and then dropped into a copper calorimeter of mass 400 gram containing 400 gram of water initially at 20°C. If the final equilibrium temperature of the system is 22.4°C, find the specific heat of the metal. Specific heat of copper is 386 J kg<sup>1</sup> K<sup>-1</sup>.

#### Data

 $m_M$  = mass of Metal =  $m_M$  = 50g = 0.05kg c = Specific heat of the metal c = ?  $T_M$  =Temperature of the metal piece =  $T_M$  = 100°C  $T_F$  = Final temperature =  $T_F$  = 22.4°C  $m_W$  = Mass of water =  $m_W$  = 400g = 0.4 kg  $m_c$  = Mass of Calorimeter =  $m_c$  = 400g = 0.4 kg  $m_c$  = Specific Heat of Water =  $m_c$  = 4200 Jkg<sup>-1</sup> K<sup>-1</sup>  $m_W$  = Initial temp: of water =  $m_W$  = 20°C

Solutions From the law of heat exchange.

Heat lost by metal = Heat gained by water + Heat gained by Calorimeter.

c = Specific heat of Copper = c = 386 J kg<sup>-1</sup> K<sup>-1</sup>

or

$$m_{M} \times c \times (T_{M} - T_{F}) = m_{W} \times C_{W}(T_{F} - T_{W}) + m_{C} c(T_{F} - T_{W})$$
.05kg xcx(100-22.4)K=0.4kg x4200J/kg<sup>-1</sup>K<sup>-1</sup>x(22.4-20)
+ 0.4 Kg x 386 J/kg<sup>-1</sup> K<sup>-1</sup> (22.4-20)

 $c = 1(34.68)/kg^{-1}k^{-1}$ 

## 11.15. Molar Specific Heat

As a matter of convenience mole is often used to describe the amount of substance. One mole of any substance is defined as the quantity of matter such that its mass in gram is numerically equal to the molecular weight M. If n is the number of moles and m is the mass in gram of the substance, then

For specific heat we have the relation

$$c = \frac{\Delta Q}{m\Delta T} \qquad (11.29)$$

Substituting the mass m in 11.29 by nM from 11.28, we get

$$C = \Delta Q/nM \Delta T$$

$$M_c = \Delta Q/n \Delta T \qquad (11.30)$$

The product M<sub>c</sub> of molecular weight and specific heat is called the molar specific heat and is defined as the quantity of heat required to raise the temperature of one mole of a substance through 1 K. Its units are J-mole<sup>-1</sup>K<sup>-1</sup>.

The molar specific heat of a gas depends upon whether or not the gas allowed to expand when it is heated. When the volume of the gas is kept constant throughout heating we call it the molar specific heat at

constant volume. It is defined as the amount of heat energy required to raise the temperature of one mole of a gas through 1 K at constant volume. It is designated by the symbol C<sub>v</sub>. When the volume of the gas is allowed to increase but its pressure is kept constant throughout heating, we speak of the molar specific heat at constant pressure. It is defined as the amount of heat energy required to raise the temperature of one mole of a gas through 1 K at constant pressure and it is denoted by the symbol C<sub>p</sub>.

## 11.16. Heat and Work in Thermodynamics

Laws governing the conversion of energy to and from heat and the methods employed for such transformations are the subject matter of thermodynamics. Before going in the details of these laws, let us briefly describe the treatment of heat and work in thermodynamics.

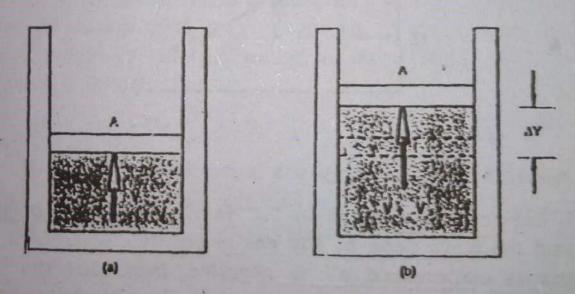


Figure 11.6 Gas contained in a cylinder at a pressure p does work on a moving piston as the system expands from a volume  $v = \Delta v$ Fig:11.6

Consider a thermodynamic system such as a gas contained in a cylinder fitted with a movable piston (Fig.11.6). In equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder walls and piston. If the piston has a cross section area A, the

force exerted by the gas on the piston is F= PA. Now let us assume that the gas expands slowly. till it attains the equilibrium state.

As the piston moves up a distance Dy, as shown in fig. 11.6(b) the work done by the gas on the system is

$$\Delta W = F\Delta Y = PA \Delta Y$$

Since AAY is the increase in volume of the gas, AV, we can express the work done as

$$\Delta W = P\Delta V$$
 ----(11.31)

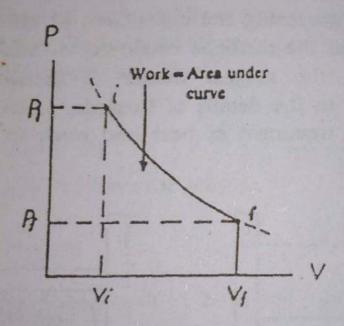


Fig:(11.7.)

If the gas expands, as in Fig. (11.7) then  $\Delta V$  is positive and the work done by the gas is positive, whereas if the gas is compressed  $\Delta V$  is negative, indicating that the work done by the gas is negative. (In the latter case, negative work can be interpreted as work being done on the system). Clearly, the work done by the system is zero when the volume remains constant. The total work done by the gas as its volume changes from  $V_i$  to  $V_i$  can be expressed by the area under the curve in a diagram (Fig.11.7), from Fig. 11.7 the work done in the expansion from the initial state "i", to the final state "f", will depend on the specific path taken between these two states.

# 11.17. The First Law of Thermodynamics

Let there be a system which absorbs  $\Delta Q$  amount of heat and as a consequence of this it performs  $\Delta W$  amount of work. In this process the initial equilibrium state "I" of the system changes to a final equilibrium state "I" in a particular way and  $\Delta Q$  -  $\Delta W$  is computed. Now this system is changed from the same initial state "I" to the final state "J" but along a different path. This procedure is repeated many times. It is observed that  $\Delta Q$  -  $\Delta W$  comes out the same in all cases inspite of the fact that  $\Delta Q$  and  $\Delta W$  separately depend on the path taken.  $\Delta Q$  -  $\Delta W$  depends only on the initial and final states.

aQ is the energy added to the system and W is equal to the energy that has been extracted, from the system by the performance of work. The difference ΔQ - ΔW which is retained within the system is the change in the energy of the system. It follows that the initial energy change of a system is independent of the path and is therefore equal to U<sub>1</sub>, internal energy of the system in state "f" minus the internal energy in state "i" or U<sub>1</sub> - U<sub>1</sub>. Therefore, it follows that

$$\Delta Q - \Delta W = U_{1} - U_{1} = \Delta U$$
 ----(11.32)

The change in internal energy of a system in any process is equals to net heat flow into the system minus the total work W done by the system.

# 11.18. Special Cases

let us look at some special cases. First consider an isolated system, that is, which does no external work and there is no flow of heat. Then for any process taking place in such a system  $\Delta W$ -  $\Delta Q$  = 0 and  $U_2$  -  $U_1$  = 0 or  $\Delta U$  = 0 which says that the internal energy of a system remains constant. This is the most general statement of the conservation of energy. The internal energy of an isolated system cannot be changed by any process

(mechanical, electrical, chemical, or biological) taking place within the system. The energy of a system can be changed only by a flow of heat across its boundary or by the performance of work.

Next consider a process in which the system is taken through a cyclic process, that is, one that starts and ends up at the same state. In this case the change in internal energy is zero.i.e.

$$U_2 = U_1$$
 and  $\Delta Q = \Delta W$ 

Thus, although net work W may be done by the system in the process energy has not been created, since an equal amount of energy must have flown into the system as heat  $\Delta Q$ .

### Example 11.6.

A system absorbs 1000 Joules of heat and delivers 600 joules of work while losing 100 Joules of heat by conduction to the atmosphere. Calculate the change in the internal energy of the system.

#### Solution

$$\Delta U = \Delta Q - \Delta W$$

$$\Delta Q = + 1000 \text{ J} - 100 \text{ J} = + 900 \text{ J}$$

$$\Delta W = 600 \text{ Joules}$$
therefore.  $\Delta U = 900 \text{ J} - 600 \text{ J} = 300 \text{ J}$ 

#### Example 11.7.

A thermodynamic system undergoes a process in which its internal energy decreases by 300 J. If at the same time, 120 J of work is done on the system, find the heat transferred to or from the system.

#### Solution

$$\Delta U = \Delta Q - \Delta W$$

$$300 J = \Delta Q - 120 J$$

$$420 J = \Delta Q$$

gince this amount of heat leaves the system

So  $\Delta Q = -420 \text{ J.}$ 

# 11.19. Applications of First Law of Thermodynamics

Let us consider the following cases.

# 1. Isobaric Process

at constant pressure. In such a process the heat transferred and the work done are both non-zero. When water enters the boiler of a steam engine and is heated to its boiling point, vaporized, and then the steam is superheated, all these processes take place isobarically. Such processes play an important role in mechanical engineering and also in chemistry.

In Fig.11.8. (a,b,c) we show an isobaric process. The system is a gas contained in a cylindrical vessel provided with frictionless air tight piston and is free to move. An infinitesimal heat  $\Delta Q$  is transferred from the surroundings to the system. The gas expands such that the external pressure p remains unchanged as shown in Fig.11.8. (c). The work done by the gas in moving a piston of area A to a small distance  $\Delta x$  is given by:

 $\Delta W = F \times \Delta x$   $= (PA) \Delta x$   $= P \Delta V$ 

Where  $\Delta V$  is the increase in the volume of the gas from volume  $V_1$  to volume  $V_2$ . So we can also write the above equation as:

 $\Delta W = P(V_2 - V_1)$  ----(11.33)

Substituting this value of W in the relation  $Q-W=\Delta U$  we get

 $\Delta Q = P(V_2 - V_1) + \Delta U$  -----(11.34)

This is the form of 1st law of thermodynamics in an iso-

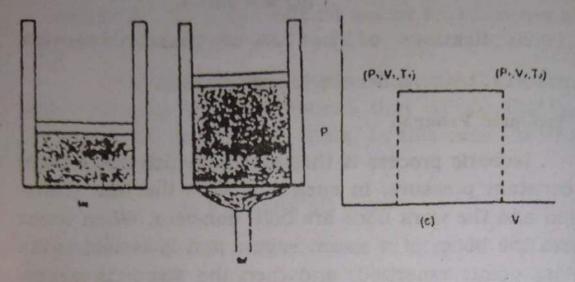


Fig. (11.8) abc

#### 2. Isochorle Process

Isochoric process is defined as that process in which the volume of the system remains constant.

Consider a cylinder fitted with a piston containing a certain amount of gas. It is heated by supplying an amount of heat  $\Delta Q$  keeping its volume fixed. During this heating the pressure of the gas increases from  $p_1$  to  $p_2$  (Fig. 11.9). Since there is no change in the volume of the gas, so the work done W is zero. From the first law of thermodynamics, putting W = 0, we get

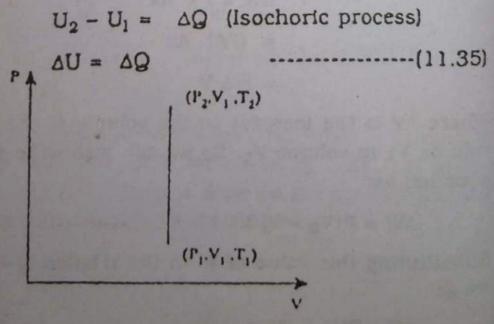


Fig.(11.9.)

# 3. Isothermal Process

If the temperature of the system remain constant throughout the process, it is called an isothermal process.

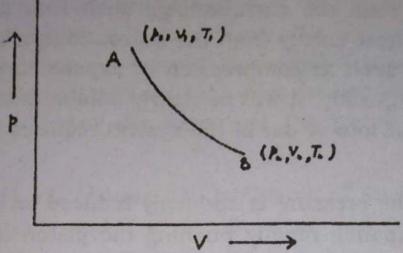


Fig. (11.10)

The pressure, temperature and volume of a gas in a cylinder is shown in (Fig.11.10) by point A. The cylinder has a heat conducting base and non conducting walls and piston and it is placed on a heat reservoir, a body of large heat capacity at a constant temperature T<sub>1</sub>. If the pressure of the gas in the cylinder is decreased by decreasing the weights on the piston there should be a fall in temperature. But since the system is perfectly conducting to the reservoir it will absorb heat from the reservoir and maintain a constant temperature from A to B. In order to keep temperature of the gas constant, the changes in its pressure and volume must be carried out very slowly.

The internal energy of the gas does not change during this process i.e.  $U_2 - U_1 = 0$ . Therefore from the first law of Thermodynamics.

$$\Delta Q = \Delta W$$
 (Isothermal process)----(11.36)

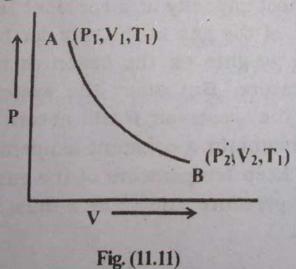
Eq.11.36 represents the 1st law of thermodynemics in an isothermal process and the curve in Fig 11.10. is called an isotherm.

#### 4. Adiabatic Process

The process in which no heat flows into or out of the system is called an adiabatic process. During an adiabatic process, the working substance is perfectly insulated from the surroundings such that it does not exchange heat energy from the surroundings. However, if a process such as compression or expansion of a gas is done very quickly, it will be nearly adiabatic because the flow of heat into or out of the system requires finite time.

If the pressure is suddenly reduced on the piston, the gas expands rapidly pushing the piston up and the temperature falls. As no heat exchange can take place, the first law of thermodynamics reduces to  $\Delta U = -\Delta W$  -----(11.37)

A curve between pressure and volume during the adiabatic process is called an adiabatic curve or an adiabatic as shown in Fig. 11.11.



## 11.20. Derivation of Cp - Cv = R

When we heat a substance, its temperature rises under various conditions, for example, the volume may be kept constant or the pressure may be kept constant or both may be allowed to vary in some definite manner. In each of these cases, the amount of heat required per mole per unit rise of temperature (we define this as the

molar heat capacity) is different. Only two kinds of molar heat capacities are important for gases, namely, that at constant volume C<sub>V</sub>, and that at constant pressure C<sub>P</sub>.

Let us consider a piston cylinder arrangement having a certain number of moles of an ideal gas. The cylinder is placed on a heat reservoir, the temperature of which can be raised or lowered as needed. The gas has a pressure p such that its upward force on the frictionless piston just balances the weight of the piston and its load.

Fig. 11.12. shows two isotherms of an ideal gas at temperature T and T +  $\Delta$ T. Suppose that the gas is taken along the constant pressure path a  $\longrightarrow$  b in figure (11.12). The temperature also increases by  $\Delta$ T along this path. The heat transferred to the gas in this process is given by  $\Delta$ Q =  $\alpha$ Cp  $\Delta$ T, where Cp is the molar heat capacity at constant pressure. We note that the volume increases in this process. We call this increase as  $\Delta$ V. So the work done by the gas is W =  $\Delta$ PDV. Applying the first law to this process, we have

 $\Delta U = \Delta Q - \Delta W.$   $= n C p \Delta T - P \Delta V \qquad (11.38)$ 

The temperature of a given mass of gas is raised by the same amount by a constant volume process (a -c).

Apply the equation of state PV = nRT to the constant pressure process a — b. For P constant we have, taking PΔV = nRΔT, Eq. (11.38) reduces to

$$\Delta U = n C_p \Delta T - nR \Delta T \qquad -----(11.39)$$

Let us consider the constant volume process that carries the system along the path  $a \rightarrow c$  (Fig. 11.12). By definition  $Q = n C_v \Delta T$ , where  $C_v$  is the molar heat capacity at constant volume.

Also since  $(\Delta V = 0$ , so  $\Delta W = p \Delta V)$  is also zero. Therefore from the first law of thermodynamics.

Q-W= AU. We have

 $\Delta U = n C_v \Delta T$ 

substituting this into equation (11.39), we get  $n C_p \Delta T = n C_v \Delta T + n R \Delta T$ 

Which gives

$$C_p - C_v = R$$
 -----(11.40)

This expression applies to any ideal gas. It shows that the heat capacity of an ideal gas at constant pressure is greater than the heat capacity at constant volume by an amount R, the universal gas constant (8.313 J mof.K-1)

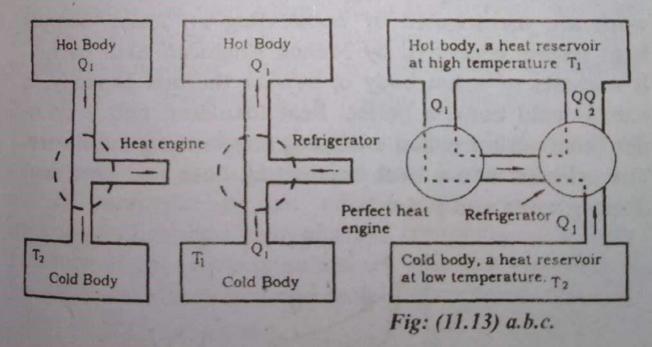
## 11.21. The Second Law of Thermodynamics

energy is called heat engine. The essentials of a heat engine are the furnace, or hot body, the working substance and a condenser or cold body. In a steam engine, the steam absorbs heat from the furnace, converts some of it into work by applying pressure to the piston and rejects the rests to the condenser. The point to note is that the furnace is at a higher temperature than the condenser and this conversion of heat into work is possible when the working substance falls in temperature as shown in Fig 11.13(a). We can generalise it by sayin that the two

bodies must be maintained at different temperatures for the working of a heat engine. A continuous supply of work has never yet been obtained from a single supply of heat otherwise we could build a ship which would use far more heat in the ocean water without needing any fuel. This leads to the first way of stating the second law of thermodynamics due to Kelvin.

"It is impossible to derive a continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surrounding".

Let us consider the fact that no one has ever built a refrigerator which will work without a supply of energy. A refrigerator is essentially a machine for conveying heat from one body at a lower temperature to another at a higher temperature as shown in Fig 11.13 (b). In other words, it is only possible to make heat flow from a cold body to a hot body by using up work. The statement of second law of thermodynamics due to Clausius comes from the consideration of this fact of refrigerator and it is stated.



"It is impossible to cause heat to flow from a cold body to a hot body without the expenditure of energy".

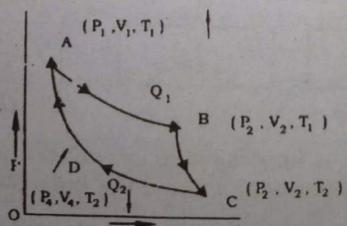
We shall now prove that both these statements are equivalent by showing that if either of these state-

ments is supposed to be false, the other must be false also. We suppose that Kelvin's statement is false then we could have a heat engine which takes heat from a source and converts it completely into work. If we connect this perfect heat engine to an ordinary refrigerator we can take heat from the hot body and convert it completely to work. This work can be used to operate the refrigerator which conveys heat from the cold body to the hot body. The net result is a transfer of heat from a cold body to a hot body without the expenditure of work which is contrary to Clausius' statement.

According to Kelvin statement, an engine, when converting heat into mechanical work, can not convert all of it into work. A part of the heat must be rejected to a cooler reservoir, the exhaust. In other words, it is impossible to device a machine that would have an efficiency of 100 percent, even though the first law will be satisfied.

# 11.22. The Carnot Engine

The law, governing the conversion of heat into work are investigated by considering an ideally simple heat engine conceived by French Engineer, Sadi carnot. It consists of a hot body of infinite thermal capacity, a similar cold body, a perfect heat insulator, and a cylinder fitted with a piston enclosing any working substance. The cylinder has a heat conducting base and non conducting walls and piston.



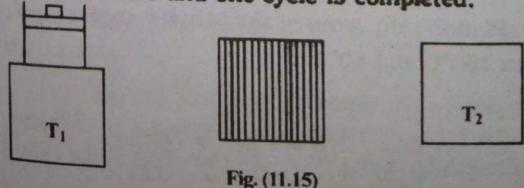
20

The working substance is taken through the following cycle of operations known as the carnot cycle (Fig. 11.14). Starting at the condition shown by the point A, the cylinder is placed on a hot body (Fig. 11.15) at temperature T<sub>1</sub> and the load on the piston is decreased in order to allow the gas to expand very slowly at temperature T<sub>1</sub>. This expansion is strictly isothermal as the bottom of the cylinder is a perfect conductor and the thermal capacity of the hot body is infinite. It is allowed to continue until the volume of the substance reaches the point B, when the cylinder is taken to be perfect heat insulator.

The gas is allowed to expand and this expansion is adiabatic since no heat can enter or leave the system. This expansion is shown along BC and the temperature of the gas falls from  $T_1$  to  $T_2$ .

The cylinder is removed from the insulator and is placed on the cold body at a temperature T<sub>2</sub> and the working substance is compressed very slowly by putting the weight on the piston just greater than the force due to the pressure of the working substance. During this compression the heat energy Q<sub>2</sub> is transferred from the gas to the cold body through the conducting base. The working substance undergoes isothermal expansion shown by CD and some work is done on the gas.

When the point D is reached, the cylinder is once again put back on to the perfect heat insulator. The cycle is completed by an adiabatic compression DA because no heat can leave or enter the system. The temperature of the working substance has risen to that of hot body once more and one cycle is completed.



If Q<sub>1</sub> is the heat absorbed by the working substance from the hot body in the isothermal expansion AB and Q<sub>2</sub> is the heat rejected to the cold body during isothermal compression CD, and W is the external work done by the engine in one cycle, then from the first law of thermodynamics

$$W = Q_1 - Q_2$$
 ----- Eq. (11.41)

In this cycle, the system comes back to its initial state and hence, there is no change in its internal energy. The efficiency E of a heat engine is defined as

$$E = \frac{\text{output}}{\text{input}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} - \dots - (11.42)$$

Eq. 11.42. shows that the efficiency of the engine increases as the ratio  $Q_2/Q_1$  decreases. It can also be proved that heat transferred to or from a carnot engine is directly proportional to the temperature of the hot or cold body:

$$Q_2/Q_1 = T_2/T_1$$
 ----(11.43)

Thus the efficiency of the carnot engine can be written

efficiency = 
$$1 - \frac{T_2}{T_1}$$
 . .....(11.44)

It is thus concluded from Eq.11.44 that the smaller the ratio  $T_2/T_1$  the more is the efficiency.

## Example 11.8.

Find the efficiency of the carnot's engine working between 150°C and 50°C.

Solution

$$T_1 = 273 + 150 = 423 \text{ K}$$
 $T_2 = 273 + 50 = 323 \text{ K}$ 

$$c = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{323}{423} = 100/423 = .236$$

efficiency = 23.6%

11.23. Entropy and the Second Law of Thermodynamics

# ENTROPY

we introduce here another new concept known as entropy. We may say that entropy is a measure of molecular disorder and in any process the entropy increases or remains constant, that is the disorder increases or remains constant.

In order to explain this let us consider a large number of molecules of a gas confined in an insulated cylinder fixed with a removable partition as shown in fig 11.16 (a). To start with all the molecules are confined in a volume V = V, we say that the molecules are localized within a volume V. Suppose now that the partition is removed. The molecules instead of staying confined to volume V, now occupy the whole volume  $V_2 = 2V$ , as shown in fig 11.16 (b) and are less localized then they were before the partition was removed. Actually, the degree of localization is a measure of disorder. As the system increases in volume, the disorder increases, and we say that the entropy increases. Also, there is almost no chance that all the molecules by themselves will collect in the original volume. V1. That is why we made the statement "entropy or disorder always increases are remains constant."

We take here another example of the increase of the disorder of a system. Consider equal number of black and white balls contained in a box. The black balls occupy one half of the box while the white balls occupy the other half of the box. We would say that the balls are placed in order. As we shake the box this order of the black and white balls is disturbed. As the box is shaken more, the order is disturbed more. We can say that the disorder increases and the original arrangement cannot be restored no matter how we shake the box.

Scientists describe such a situation by saying that the entropy of the system has increased. These considerations thus lead to define the second law of thermodynamics as follows:

"When an isolated system undergoes a change, the disorder in the system increases".

As said above, entropy is thought of as being synonymous with the 'degree of disorder'. The second law of thermodynamics is then also defined as:

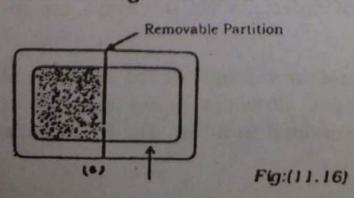
> "When an isolated system undergoes a change, the entropy of the system either remains constant or it increases"

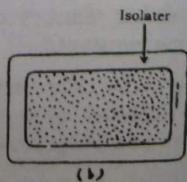
It is our experience also that the natural tendency of the things is to go into disordered state.

If  $\Delta Q$  be the heat transferred to a system at constant kelvin temp T, then

Change in entropy 
$$\Delta S = \frac{\Delta Q}{T}$$
 ----- (11.45)

If heat is removed from a body, the change in entropy is written as negative. Its SI unit Jk-1





#### QUESTIONS

- 11.1. How do you distinguish between temperature and heat? Give examples.
- 11.2. Why the earth is not in thermal equilibrium with the sun?
- 11.3. Is temperature a microscopic or macroscopic concept?
- 11.4. It is observed that when a mercury in a glass thermometer is put in a flame, the column of mercury first descends and then rises. Explain.
- 11.5. Is it correct that unit for specific heat capacity is  $m^2 S^2 (C^{\circ})^{-1}$ ?
- 11.6. What is the standard temperature?
- 11.7. When a block with a hole in it is heated, why does not the material around the hole expand into the hole and make it small?
- 11.8. A thermometer is placed in direct sunlight. Will it read the temperature of the air, or of the sun, or of some thing else.
- 11.9. Will kilogram of hydrogen contain more atoms than kilogram of lead? Explain.
- 11.10. The pressure in a gas cylinder containing hydrogen will leak more quickly than if it is containing oxygen. Why?
- 11.11. What are some factors that affect the efficiency of automobile engines?
- 11.12. What happens to the temperature of a room in which an air conditioner is lest running on a table in the middle of the room.
- 11.13. When a scaled thermos bottle full of hot coffee is shaken, what are the changes, if any in

- a) the temperature of the coffee and
- b) the internal energy of the coffee.

#### PROBLEMS

- 11.1. i) The normal body temperature is 98.4 F. What is this temperature on Celsius scale?

  (Ans: 36.88°C)
  - II) At what temperature do the Fahrenheit and Celsius scales coincide. Ans 40°.
- 11.2. A steel rod has a length of exactly 0.2 cm at 30°C. What will be its length at 60°C?

  (Ans: 0.20066 cm).
- 11.3 Find the change in volume of an aluminium sphere of 0.4m radius when it is heated from 0 to 100°C.

  (Ans: 0.0019 m<sup>3</sup>).
- 11.4 Calculate the root mean square speed of hydrogen molecule at 800K. (Ans: 3158.6 ms<sup>-1</sup>).
- ergy of the partieles of an ideal gas at 0°C and at 50°C.

  (Ans: 5.65 x 10<sup>-21</sup>J), (6.68 x 10<sup>-21</sup>J)
  - b) What is the kinetic energy per mole of an ideal gas at these temperatures?

    (3404.5 J/mole), (4026.2 J/mole).
- 11.6. A 2 kg iron block is taken from a furnace where its temperature was 650°C and placed on a large block of ice at 0°C. Assuming that all the heat given up by the iron is used to melt the ice, how much ice is melted. (Ans: 1.93 kg).
- 11.7. In a certain process 400 J of heat are supplied to a system and at the sametime 150J of work are done by the system. What is the increase in the

internal energy of the system.(250J)

- joules when 800 joules of work is done by a system. What is the amount of heat supplied during this process?

  (Ans: 1200 J).
- 11.9. A heat engine performs 200J of work in each cycle and has efficiency of 20 percent. For each cycle of operation a) How much heat is absorbed and b) How much heat is expelled?
  - a) (Ans: 1000 J) (b) (800 J)
- 11.10. A heat engine operates between two reservoirs at tem.
  peratures of 25°C and 300°C. What is the maximum
  efficiency for this engine? (Ans: 48%)
- 11.11 The low temperature reservoir of a carnot engine is at 7°C and has an efficiency of 40%. It is desired to increase the efficiency to 50%. By how much degrees the temperature of hot reservoir be increased.

  (Ans: 93.4 K)