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(University with Potential for Excellence)



DIRECTORATE OF DISTANCE EDUCATION

B.Sc., Physics

PAPER - II

**HEAT, THERMODYNAMICS &
STATISTICAL MECHANICS**

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B.Sc. Physics

Paper - II

**HEAT, THERMODYNAMICS &
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Paper – II Heat , thermodynamics & statistical mechanics

Unit I

Isothermal and adiabatic changes . Definition – Specific heat capacity (C_v and C_p) – derivation of equations for both C_v and C_p of gas – relation between C_p and C_v . Calorimetry – Joly's differential steam calorimeter for finding C_v – Callender and Barnes continuous flow method to determine C_p .

Unit II

Kinetic theory of gases – Mean free path – Transport phenomena – Diffusion, viscosity and thermal conductivity. Maxwell's law of distribution of molecular velocities (no derivation) – expression for mean free velocity, mean square velocity, most probable velocity – experimental verification by toothed wheel method. Degree of freedom – Law of equipartition of energy – Liquefaction of gases – Liquefaction of air by Linde's method – properties of Helium I and II – Adiabatic demagnetization.

Unit III

Transmission of heat – thermal conductivity – thermal diffusivity – Rectilinear flow of heat – Ingen Hausz experiment – Lees disc method of determination of thermal conductivity of bad conductor. Radiation – Black body Radiation – Wien's law, Reyleigh Jeans law and Plank's law (no derivation) Stefan's law and its experimental verification – solar constant and experimental determination.

Unit IV

Zeroth first law of thermodynamics – Reversible and irreversible process – Second law of thermodynamics – Carnot's engine – derivation of efficiency – Carnot's theorem statement – Entropy – changes of entropy in reversible and irreversible process – changes of entropy in conversion of ice into steam. Third law of thermodynamics.

Unit V

Probability – phase space – elements of phase space – macro state and macro state probability distribution – Fundamental postulates of statistical mechanics – entropy and probability – elementary ideas of Maxwell Boltzmann, Fermi – Dirac and Bose Einstein statistics.

Text Book

1. Heat and thermodynamics by Brijilal and Subramanian, S. chand & Co. 1999
2. Elements of Mechanics D. S. Mathur, 1999, Tata McGraw Hill

Reference Book

1. Thermal Physics – R. Murugesan, S. chand & Co
2. Fundamentals of Statistical mechanics A. K. Dasgupta NCBA (p) LTD, Calcutta

Paper – II Heat , thermodynamics & statistical mechanics

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UNIT 1

Structure

- 1.1 Introduction
- 1.2 Objectives
- 1.3 Isothermal and adiabatic changes
- 1.4 Specific Heat Capacity (C_v and C_p)
- 1.5 Relation between C_p and C_v
- 1.6 Calorimetry
- 1.7 Jolly's differential steam calorimeter to determine C_v
- 1.8 Callender and Barnes continuous flow method to determine C_p
- 1.9 Let us sum up
- 1.10 Unit – end exercises
- 1.11 Problems for discussion
- 1.12 Answers to check your progress and problems
- 1.13 Suggested readings

1.1 Introduction

Thermodynamics is the branch of Physics which is mainly concerned with the transformation of heat into mechanical work. It involves the study of the interaction of one body on another in terms of the quantities heat and work. The study of the thermal energy is often called the internal energy of the system with the main concept of temperature. Thermodynamics has nothing to say about atoms but only concerned with macroscopic variables such as pressure, volume and temperature.

The properties of many bodies change as we alter their temperature. When a body is heated its temperature rises. The rise in temperature depends on the quantity of heat given to the body and the nature of its materials. The quantity of heat required is specific heat of substance and is not constant. Specific heat of a gas can be considered by taking any one of the two variables (either pressure or volume) as constant. The internal energy of the system is single valued function of the state variables *viz.*, pressure, volume, temperature *etc.*, In the case of gas, any two of the variables P , V , T are sufficient to define completely its state. In this unit, we are going to learn about isothermal and adiabatic changes, definition and relation between C_p and C_v and the experiments to determine C_p and C_v .

1.2 Objectives

After studying this unit you will be able to

- explain isothermal and adiabatic process
- define C_p and C_v
- derive Mayer's relation connecting C_p and C_v

- describe the Joly's differential steam calorimeter for finding C_v and
- explain the working of Callender and Barnes continuous flow method to determine C_p .

1.3 Isothermal and adiabatic changes

1.3.1. Isothermal Process

Definition:

When a change in the pressure and volume of a given mass of gas takes place at constant temperature, the process is called an isothermal process.

Explanation:

Consider a gas contained in a cylinder and compressed by a piston (Fig. 1.1). The piston moves very slowly. The walls of the vessel and the piston are good conductors.

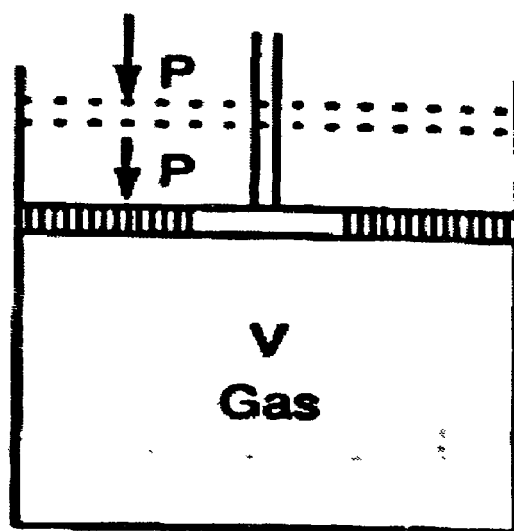


Fig. 1.1

Then, the gas will be at the same temperature throughout. The work done on the gas is converted into heat in the gas. This heat is conducted away by the cylinder and the piston to the surrounding air outside. The compression in this case is isothermal, *i.e.* at constant temperature.

The curves representing the variation in the volume of a substance when the pressure acting on it changes under isothermal conditions are called isothermals (Fig. 1.2).

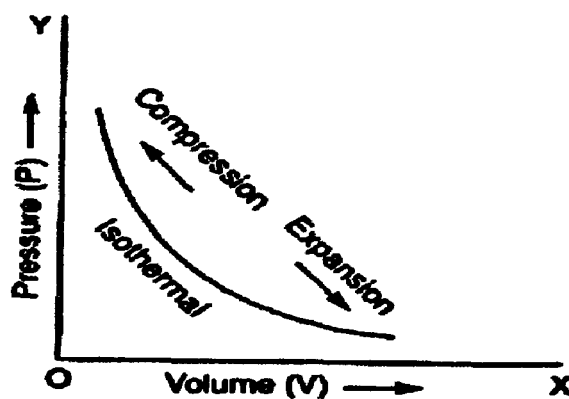


Fig. 1.2

In an isothermal process, the equation connecting P and V of one mole of a gas is

$$PV = RT = \text{const.}$$

For n moles of gas, we have

$$PV = n RT$$

1.3.2 Adiabatic Process

Definition:

An adiabatic process is a process in which changes in volume and pressure of a given gas takes place in complete thermal isolation. During an adiabatic process, no heat enters or leaves the system, but the temperature changes.

Explanation:

Consider a gas enclosed in a cylinder, fitted with a piston (Fig. 1.3).

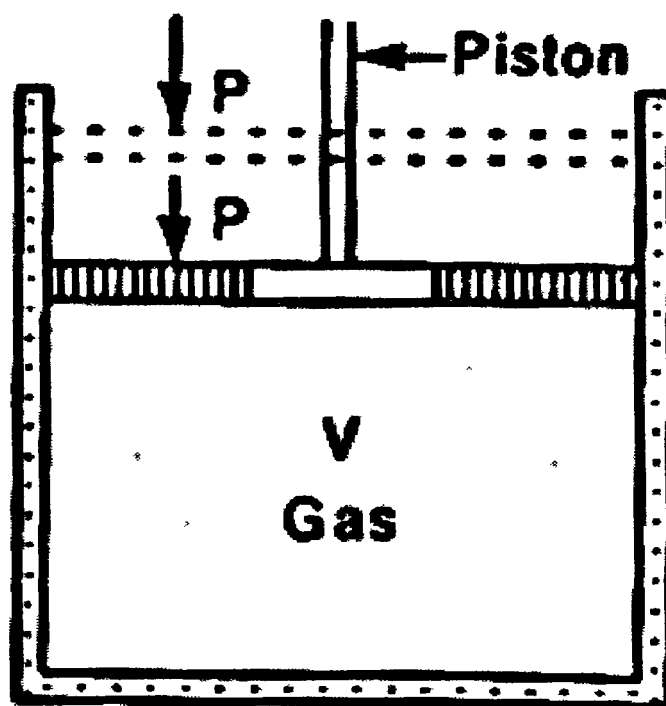


Fig. 1.3

Assume that both the cylinder and piston are perfect insulators of heat. If the gas is suddenly compressed, the temperature of the gas increases. Similarly, if the gas suddenly expands, its temperature falls. Thus, there is no exchange of heat between the gas and surroundings.

Examples:

- 1 The compressions and rarefactions produced in air during the propagation of sound waves is an example of adiabatic process.
- 2 The sudden expansion of the enclosed air into the atmosphere, when a motor tyre bursts, is approximately adiabatic. Hence the tyre is cooled.
- 3 The compression of the mixture of oil vapor and air during compression stroke of an internal combustion engine is an adiabatic process and there is rise in temperature.

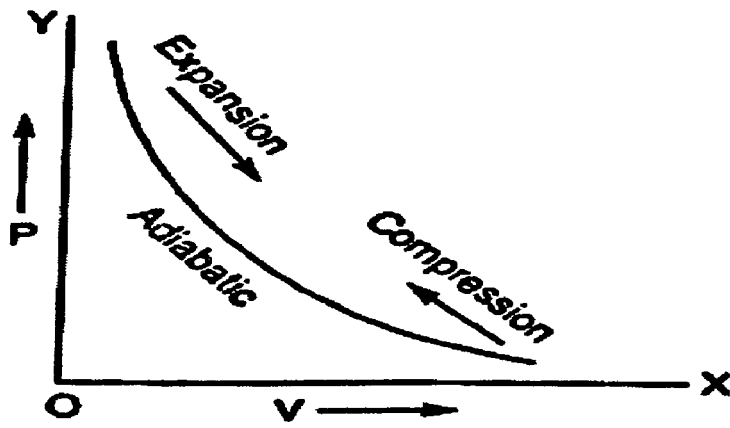


Fig 1.4

A curve showing the variation in the volume of a gas when the pressure acting on it changes under adiabatic conditions is called an adiabatic (Fig. 1.4). For an adiabatic change in a perfect gas, $dQ = 0$. Hence, from the first law of thermodynamics,

$$dU + dW = 0$$

$$dU = -dW$$

1.3.3 Gas Equation during an Adiabatic Process

Let a quantity of heat dQ be supplied to 1 mole of a perfect gas. The heat is used for (i) increasing the temperature of the gas by dT and (ii) doing external work for the expansion of the gas, $P dV$ (Fig. 1.5).

$$dQ = C_v dT + P dV$$

In an adiabatic change, no heat is supplied from outside. Hence $dQ = 0$.

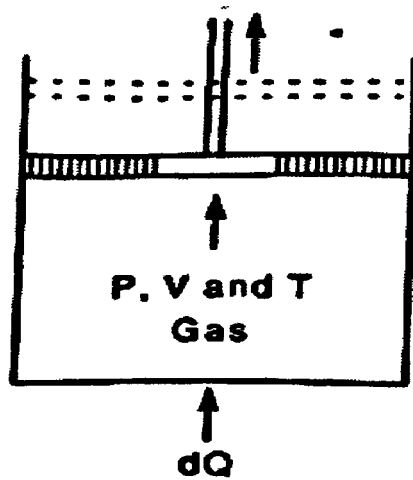


Fig. 1.5

Therefore, we have

$$C_v dT + P dV = 0 \quad (1)$$

For one mole of a perfect gas, $PV = RT$.

Differentiating, $P dV + V dP = R dT$

$$dT = \frac{P dV + V dP}{R} \quad (2)$$

Substituting this value of dT in Eq. (1),

$$C_v \left(\frac{PdV + VdP}{R} \right) + PdV = 0$$

or $C_v P dV + C_v V dP + RPdV = 0$

or $C_v P dV + C_v V dP + (C_p - C_v)PdV = 0$ [since, $C_p - C_v = R$]

or $C_v V dP + C_p P dV = 0$

Dividing by $C_v PV$, $\frac{dP}{P} + \frac{C_p}{C_v} \frac{dV}{V} = 0$

But $C_p / C_v = \gamma =$ Ratio of the principal specific heat capacities of the gas.

Hence, $\frac{dP}{P} + \gamma \frac{dV}{V} = 0$ (3)

Integrating, $\log_e P + \gamma \log_e V = \text{constant}$

or $\log_e PV^\gamma = \text{constant}$

or $PV^\gamma = \text{constant}$

This is the equation connecting pressure and volume during an adiabatic process.

Relation between pressure and temperature

We have, $PV^\gamma = \text{constant}$ (1)

For a perfect gas, $PV = RT$ or $V = RT / P$

Substituting for V in Eq. (1), $P \left(\frac{RT}{P} \right)^\gamma = \text{constant}$

or $\frac{T^\gamma}{P^{\gamma-1}} = \text{constant}$ or $\frac{P^{\gamma-1}}{T^\gamma} = \text{constant}$ (2)

Relation between volume and temperature

We have, $PV^\gamma = \text{constant}$ (1)

For a perfect gas, $PV = RT$ or $P = RT / V$

Substituting for P in Eq. (1), $\left(\frac{RT}{V} \right) V^\gamma = \text{constant}$

or $TV^{\gamma-1} = \text{constant}$ (2)

Check your progress

1. A mass of gas at 1 atmospheric pressure is compressed to 1/3 of its volume, suddenly. Find its pressure. Given γ of gas is 1.4
2. Air at N.T.P is compressed adiabatically to half of its volume. Calculate the change in its temperature.
3. Define isothermal and adiabatic changes.

Ans: -----

1.4 Specific Heat Capacity (C_p and C_v)

If a small quantity of heat dQ is required to raise the temperature of m kg of a substance from T K to $(T+dT)$ K then,

Specific heat capacity at room temperature $T = C = \frac{dQ}{mdT}$

The definition of specific heat capacity (C) given above is sufficient for solids and liquids but not for gases. Gases can be expanded or compressed easily. For a gas, C may vary between 0 and ∞ depending upon the condition under which heat is supplied.

For example if a gas is compressed, there is a rise in temperature without supplying any heat to the gas.

$$C = \frac{dQ}{mdT} = 0 \quad (\text{since, } dQ = 0)$$

On the other hand, if heat is supplied to the gas and the gas is allowed to expand such that there is no rise in temperature, then

$$C = \frac{dQ}{m \times 0} = \infty$$

Hence in order to fix the value of the specific heat capacity of a gas, either the pressure or the volume should be kept constant. Hence, we have two specific heat capacities for a gas.

$$C_v = \left(\frac{\partial Q}{\partial T} \right)_v \quad \text{and} \quad C_p = \left(\frac{\partial Q}{\partial T} \right)_p$$

Subscripts v and p indicate the parameter kept constant during the process. C_v is known as the specific heat capacity at constant volume. C_p is the specific heat capacity at constant pressure.

Definitions:

- The specific heat capacity at constant volume (C_v) is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its volume is kept constant.
- The specific heat capacity at constant pressure (C_p) is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its pressure is kept constant.

Molar heat capacity (C_m)

It is defined as the amount of heat required to raise the temperature of 1 mole of a substance through 1 K. Unit: $\text{J mol}^{-1}\text{K}^{-1}$

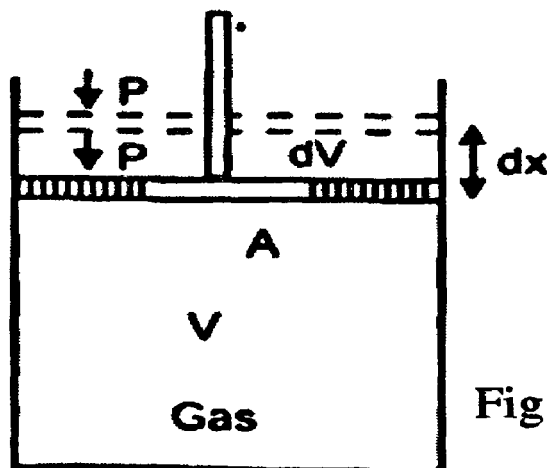
1.5 Relation between C_p and C_v

Consider one mole of a perfect gas kept in a non-conducting cylinder provided with a frictionless piston of area A (Fig. 1.6). Let T be the temperature,

V the volume and P the pressure of the gas. Let a certain amount of heat be given to the gas so that the temperature increases by dT . Assume that the piston is fixed so that the volume of the gas is constant.

Quantity of heat given to the gas = $1 \times C_v dT = C_v dT$

This quantity of heat is used in increasing the internal energy of the gas. Let us suppose that the same gas is now given a certain amount of heat at constant pressure P so that the temperature increases by dT . Since the gas is heated at constant pressure, the volume increases. The gas expands. Hence the piston moves up through a distance dx . Let dV be the increase in volume of the gas.



Quantity of heat supplied to the gas = $1 \times C_p dT = C_p dT$

This quantity of heat supplied to the gas at constant pressure is used in two ways. (i) In raising the internal energy of the gas corresponding to a raise of temperature of dT . *i.e.* by $C_v dT$. (ii) In doing the work of expanding the gas against the external pressure.

External work done by the gas in expansion

$$= \text{Force} \times \text{distance}$$

$$= PA \times dx = PdV$$

Hence,

$$C_p dT = C_v dT + P dV$$

For a perfect gas,

$$PV = RT \text{ or } P dV = R dT$$

Hence

$$C_p dT = C_v dT + R dT$$

$$C_p - C_v = R$$

This formula is known as Mayer's formula.

$R = 8.31 \text{ J mol}^{-1} \text{K}^{-1}$. In SI units, $R = 8314 \text{ J (kg mol)}^{-1} \text{K}^{-1}$. R is the universal gas constant.

Why C_p is greater than C_v ?

When a gas is heated at constant volume, the pressure increases. All the heat energy that is supplied to the gas is used in increasing the internal energy of the gas. As the volume is kept constant, no external work is done by the gas.

On the other hand, if the gas is heated at constant pressure, the volume increases. The gas expands against a constant external pressure and in so doing it

does some external work. In addition to this, there is a rise of temperature. Therefore the heat energy supplied to the gas is used in two ways.

- (i) in raising the temperature and
- (ii) in doing some external work as the gas expands.

Hence, $C_p > C_v$.

Check your progress

4. For hydrogen, the molar heat capacities at constant pressure and constant volume are 28.8 J / mole K and 20.5 J / mole K respectively. Calculate the gas constant.
5. Define C_p and C_v .
6. The molar heat capacities of a gas at constant pressure $C_p = 160$ J / mole K compute the ratio of specific heat at constant pressure to that of constant volume.
7. Does Mayer's formula apply universally?

Ans: -----

1.6 Calorimetry

(i) Heat capacity:

Substances differ from one another in the quantity of heat needed to produce a given rise of temperature in a given mass. The ratio of the heat ΔQ supplied to a body to its corresponding temperature rise ΔT is called the heat capacity of the body *i.e.*,

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

The heat capacity of a body is defined as the amount of heat required to raise the temperature of the whole of that body through 1 K. The unit of the heat capacity is JK^{-1} .

(ii) Specific heat capacity:

The heat capacity per unit mass of a body is called specific heat capacity. It is characteristic of the material of which the body is composed.

$$C = \frac{\text{heat capacity}}{\text{mass}} = \frac{\Delta Q}{m\Delta T}$$

The specific heat capacity of any substance is defined as the quantity of heat required to raise the temperature of 1 kg of the substance through 1 K. Unit $\text{J kg}^{-1}\text{K}^{-1}$.

(iii) From the definitions of heat capacity and specific heat capacity, it follows that the heat capacity of a body is equal to the product of the mass (m) of the body and the specific heat capacity (C) of the material of the body.

Heat capacity = mass \times specific heat capacity

(iv) If m is the mass of a body of specific heat capacity C , the quantity of heat energy Q required to raise its temperature through t °C is given by

$$Q = mct$$

1.7 Joly's differential steam calorimeter for finding C_v

The apparatus consists of two hollow metal spheres A and B exactly similar in volume, mass *etc.*, suspended inside the steam chamber C from the two pans of a sensitive balance. The spheres are provided with catch waters to collect the water condensed on the spheres. Two umbrella-shaped covers U_1 and U_2 prevent any water condensed on the top of the chamber from falling on the spheres. Two electrically heated coils P_1 and P_2 are placed round the suspension wires to prevent water from condensing round the narrow mouths of the steam chamber (Fig.1.7).

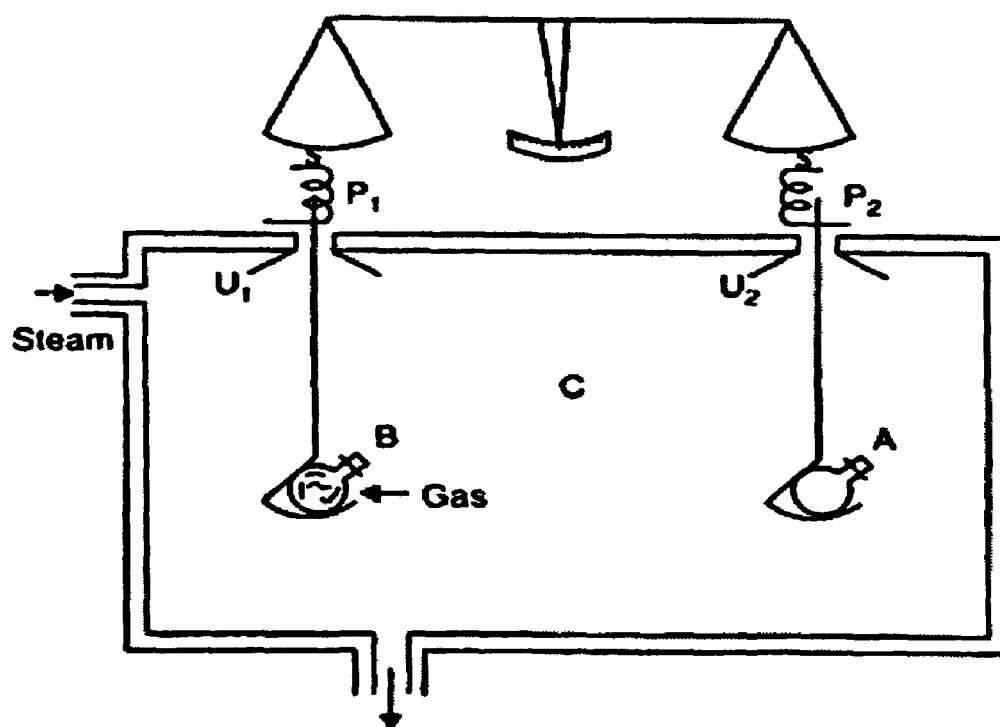


Fig. 1.7

One of the spheres is filled with the experimental gas while the other sphere is completely evacuated. By counterpoising, the mass of gas M filling one of the spheres is found. The initial temperature θ_1 of the gas is noted.

Steam is then briskly admitted into the chamber. Condensation of steam takes place on both the spheres. But more steam condenses on the sphere containing the gas than on the other because the enclosed gas also has to be heated from θ_1 to the temperature θ_2 of steam. By counterpoising the balance, the mass m of steam condensed due to the enclosed gas is found out.

Heat gained by the gas = $M C_v (\theta_2 - \theta_1)$

Heat lost by the steam = ml

Here, l is the specific heat of steam.

By the principle of method of mixtures,

$$MC_v (\theta_2 - \theta_1) = ml$$

$$C_v = \frac{ml}{M(\theta_2 - \theta_1)}$$

From this equation, the specific heat capacity of the gas at constant volume is calculated.

The experiment is repeated with the evacuated sphere filled with the gas and the other sphere exhausted. The mean of these values gives C_v .

For securing an accurate result, the following corrections must be applied.

1. The expansion of the sphere containing the gas due to increase in temperature and pressure. This may be estimated from knowledge of the expansion coefficient of copper and the initial and final pressures of the gas in the sphere.
2. Correction for the upthrust on the condensed water on the surface of the two spheres.
3. Correction for any slight difference between the thermal capacities of the two spheres.

1.8 Callender and Barnes' continuous flow method to determine C_p

The specific heat capacity of a gas at constant pressure can be determined by continuous flow method. The experimental arrangement is shown in Fig.1.8. The gas is stored up in a large copper reservoir R. It is kept immersed in a constant temperature bath W. The pressure of the gas is read by the pressure gauge G. The regulating valve V' is used for allowing the gas to flow at a constant pressure through the calorimeter D. The manometer E measures the pressure of the gas flowing through D. A heating coil C is arranged axially inside the vessel D. The current passing through the coil C is measured by ammeter A. The P.D. across the coil is measured by the voltmeter V. The incoming gas is heated due to the heat generated in the coil C. The platinum resistance thermometers T_1 and T_2

measure the temperatures of the incoming and outgoing gas. The gas travels in the direction of the arrows through the zig-zag path and finally comes in contact with the heating coil C.

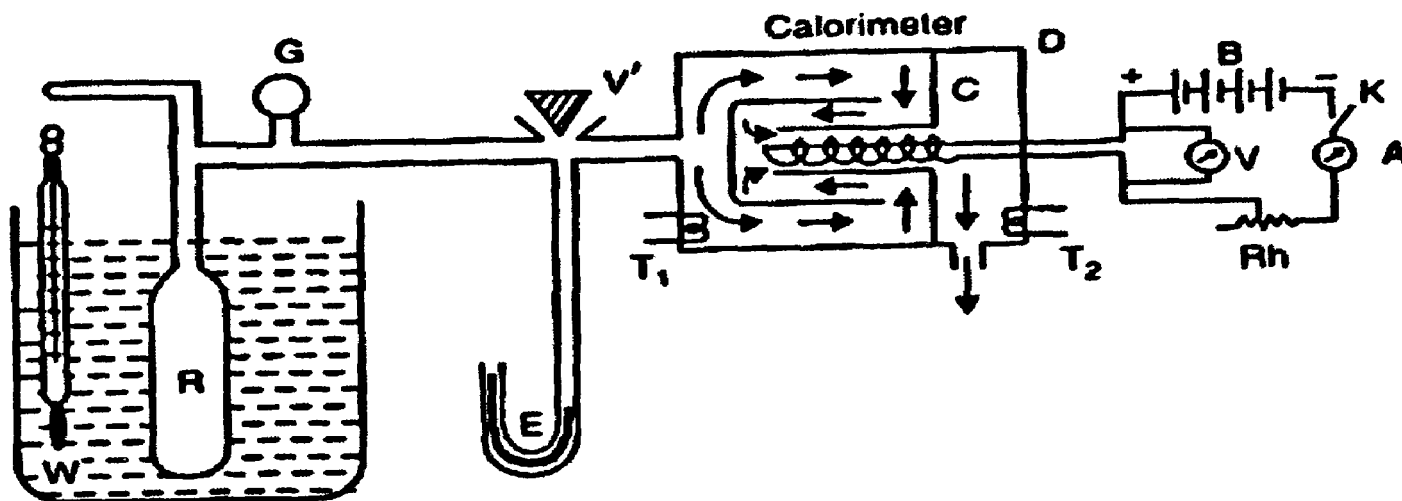


Fig.1.8

Procedure:

The gas is allowed to flow through the apparatus for some time till the steady state is reached. When the steady state is reached, the thermometers T_1 and T_2 show constant readings. Let θ_1 and θ_2 be the temperatures of the incoming and outgoing gas, as shown by T_1 and T_2 . The pressure (P_1) of the gas in the reservoir is noted by the pressure gauge G. The gas is allowed to flow through the vessel D for about 30 minutes. The final pressure (P_2) of the gas in the reservoir is needed.

Calculations:

The mass of the gas flowing out of the reservoir in t seconds is calculated from its initial and final pressures. Then,

$$\text{Heat gained by the gas} = mC_p (\theta_2 - \theta_1).$$

Let E and I be the voltmeter and ammeter readings. Then, heat produced in the heating coil in t seconds = EIt .

$$\text{Hence, } mC_p (\theta_2 - \theta_1) = EIt$$

$$C_p = \frac{EIt}{m(\theta_2 - \theta_1)}$$

To find m :

Let V be the volume of the reservoir. In the experiment $V \text{ m}^3$ of the gas at pressure $P_1 - P_2$ and temperature T has flown through the apparatus. Let V_o be the volume of the gas at N.T.P. Then,

$$\frac{(P_1 - P_2)V}{T} = \frac{0.76V_o}{273}$$

$$V_o = \frac{(P_1 - P_2)V \times 273}{0.76T}$$

Or

Let ρ_o be the density of the gas at N.T.P.

$$m = \rho_o V_o = \frac{\rho_o (P_1 - P_2) V \times 273}{0.76T} \text{ kg}$$

Thus m is known. Hence C_p can be calculated.

Advantages:

1. The radiation loss is minimized by the zig-zag arrangement for the flow of gas.
2. The temperatures of the incoming and outgoing gas are measured accurately under steady state.
3. All electrical quantities can be measured with precision. Thus the results obtained are accurate.

1.9 Let us sum up

- When a change in the pressure and volume of a given mass of gas takes place at constant temperature, the process is called an isothermal process.
- An adiabatic process is a process in which changes in volume and pressure of a given gas takes place in complete thermal isolation. During an adiabatic process, no heat enters or leaves the system, but the temperature changes.
- The equation of state for an adiabatic process,
In terms of pressure and volume, $PV^\gamma = \text{constant}$,
In terms of pressure and temperature, $\frac{T^\gamma}{P^{\gamma-1}} = \text{constant}$,
In terms of temperature and volume, $TV^{\gamma-1} = \text{constant}$.
- The specific heat capacity at constant volume (C_v) is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its volume is kept constant. $C_v = \left(\frac{\partial Q}{\partial T} \right)_v$.
- The specific heat capacity at constant pressure (C_p) is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its pressure is kept constant. $C_p = \left(\frac{\partial Q}{\partial T} \right)_p$.
- For 1 mole of a perfect gas, the difference of heat capacities C_p and C_v is equal to R ; the molar gas constant $C_p - C_v = R$
- Joly's differential steam calorimeter experiment is studied to determine C_v and
- Callender and Barnes continuous flow method is dealt to determine C_p .

1.10 Unit – end exercises

- 1 State the difference between isothermal and adiabatic changes.
- 2 Derive the equation for an adiabatic change.
- 3 What are called C_p and C_v ?
- 4 Derive Mayer's Relation.
- 5 $C_p - C_v = R$. Justify.
- 6 Describe Joly's differential steam calorimeter experiment to determine specific heat capacity at constant volume C_v . State the corrections to be followed.
- 7 Explain how the specific heat of a gas at constant pressure C_p can be determined using Callender and Barnes continuous flow method.

1.11 Problems for discussion

- 1 A quantity of air ($\gamma = 1.4$) at 27°C is compressed (i) slowly and (ii) suddenly to $1/3$ of its volume. Find the change in temperature in each case.
- 2 A motor car tyre has a pressure of 2 atmospheres at room temperature of 27°C . If the tyre suddenly bursts, find the resulting temperature. (γ for air is 1.4)
- 3 Calculate the specific heat capacity of air at constant volume; given that the specific heat capacity at constant pressure is 993 J / Kg K , density of air at N.T.P is 1.293 kg / m^3 .
- 4 Find the value of universal gas constant R for 1 mole of gas.
- 5 If the volume of each sphere of Joly's differential steam calorimeter is 500 cc and the excess of water condensed is 0.1 gm , find the specific heat of gas at constant volume. The initial temperature was 15°C and density is $6 \times 10^{-3} \text{ gm / cc}$. Latent heat of condensation of steam is $2.26 \times 10^6 \text{ J / Kg}$.

1.12 Answers to check your progress & Problems for discussion

To check your progress:

- 1 A sudden change is adiabatic. Let P_1, V_1 be the initial pressure and volume and P_2, V_2 be the final pressure and volume of the gas.

We have, $PV^\gamma = \text{constant}$

$$\text{(Or)} \quad P_1 V_1^\gamma = P_2 V_2^\gamma$$

Here, $P_1 = 1 \text{ atmosphere}, \gamma = 1.4, V_2 = \frac{V_1}{3}$

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^\gamma = 1 \times (3)^{1.4} = 4.656 \text{ atmospheres}$$

2. Let $T_1 =$ initial temperature, $T_2 =$ final temperature and $V_1 =$ initial volume,

$$\text{Final volume of the gas} = V_2 = \frac{V_1}{2}$$

During adiabatic process,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = T_1 (2)^{\gamma-1}$$

$$T_2 = T_1 (2)^{0.4} = 1.319 T_1$$

$$\begin{aligned} \text{Change in temperature} &= T_2 - T_1 \\ &= 1.319 T_1 - T_1 \\ &= 0.319 T_1 \text{K.} \end{aligned}$$

3. When a change in the pressure and volume of a given mass of gas takes place at constant temperature, the process is called an isothermal process.

An adiabatic process is a process in which changes in volume and pressure of a given gas takes place in complete thermal isolation. During an adiabatic process, no heat enters or leaves the system, but the temperature changes.

$$4. \quad C_p - C_v = R$$

$$R = (28.8 - 20.5) \text{ J / mol K}$$

$$= 8.3 \text{ J / mol K.}$$

5. The specific heat capacity at constant volume (C_v) is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K when its

$$\text{volume is kept constant. } C_v = \left(\frac{\partial Q}{\partial T} \right)_v$$

The specific heat capacity at constant pressure (C_p) is defined as the amount of heat required to raise the temperature of 1 kg of the gas through 1 K

$$\text{when its pressure is kept constant. } C_p = \left(\frac{\partial Q}{\partial T} \right)_p$$

$$6. \quad C_v = C_p - R$$

$$= (160 - 8.3)$$

$$= 151.7 \text{ J / mol K}$$

The ratio of specific heat at constant pressure to that of constant volume,

$$\gamma = \frac{C_p}{C_v} = \frac{160}{151.7} = 1.05$$

7. A real gas is made up of molecules having small but finite size and non – zero intermolecular forces. This suggests that the ideal gas law is not valid for dense gas and the equation is $C_p - C_v = R$ is approximate. This is because it makes no allowance for change in internal energy with volume. Some work has always to be done against intermolecular force

Answers To Problems for discussion:

1. (i) Since the process is isothermal there is no change in temperature.
(ii) When the air is compressed suddenly, the process is adiabatic.
Hence, $TV^{\gamma-1} = \text{constant}$
 $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\text{Here, } T_1 = 27^\circ\text{C} = 300\text{K}, \gamma = 1.4, V_2 = \frac{V_1}{3} \quad T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 300 \times (3)^{1.4-1}$$
$$T_2 = 300 \times (3)^{0.4} = 465.5\text{K}$$

$$\text{Change in temperature} = 465.5 - 300 = 165.5\text{K.}$$

2. Pressure before tyre bursts = $P_1 = 2$ atmosphere
Temperature before tyre bursts = $T_1 = 300\text{K}$
Pressure after tyre bursts = $P_2 = 1$ atmosphere
Temperature after tyre bursts = $T_2 = ?$

$$\frac{P_1^{\gamma-1}}{T_1^\gamma} = \frac{P_2^{\gamma-1}}{T_2^\gamma}$$

$$\left(\frac{T_2}{T_1} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{\gamma-1}$$

$$\left(\frac{T_2}{300} \right)^{1.4} = \left(\frac{1}{2} \right)^{1.4-1}$$

$$T_2 = (246.1 - 273) = -26.9^\circ\text{C}$$

3. $V = \text{volume per kg of air at N.T.P} = 1/1.293 = 0.7734\text{m}^3$
 $P = 0.76 \times 13600 \times 9.81 = 1.014 \times 10^5 \text{ Nm}^{-2}$ and $T = 273 \text{ K}$
Gas constant for one kg of air =

$$r = \frac{PV}{T} = \frac{1.014}{273} \times 10^5 \times 0.7734 = 287.3 \text{ J kg}^{-1} \text{ K}$$

$$C_v = C_p - r = 993 - 287.3 = 705.7 \text{ J kg}^{-1} \text{ K}$$

4. One mole of gas at N.T.P occupies 0.0224 m^3
 $P = 0.76 \text{ m of Hg} = 0.76 \times 13600 \times 9.8 = 1.013 \times 10^5$
 $V = 0.0224 \text{ m}^3, T = 273 \text{ K}$

$$R = \frac{PV}{T} = \frac{1.013}{273} \times 10^5 \times 0.0224 = 8.312 \text{ J mol}^{-1} \text{ K}^{-1}$$

5. $M = V \times \rho = (500 \times 10^{-6}) \times 6 = 3 \times 10^{-3} \text{ kg};$
 $\theta_1 = 15^\circ\text{C}; \theta_2 = 100^\circ\text{C}$
 $m = 0.1 \text{ g} = 10^{-4} \text{ kg}; l = 2.26 \times 10^6 \text{ J kg}^{-1}; C_v = ?$

$$C_v = \frac{ml}{M(\theta_2 - \theta_1)} = \frac{10^{-4} \times (2.26 \times 10^6)}{(3 \times 10^{-3})(100 - 15)} = 886.3 \text{ Jmol}^{-1}\text{K}^{-1}$$

1.13 Suggested Readings

- 1 Heat, Thermodynamics and Statistical Physics**
Brijlal, Dr. N. Subramanyam and P. S. Hemne.
Revised edition, Reprint 2012 S.Chand& Company Ltd., New Delhi
- 2 Thermodynamics and Statistical Physics**
Singhal, Agarwal, SathyaPrakash
12th edition, 2008, PragatiPrakashan, Meerut
- 3 Thermodynamics, Statistical thermodynamics and Kinetics**
Thomas Engal, Philip Reid
1st edition, 2007, Dorling Kindersley (India) Pvt Ltd, New Delhi.

UNIT 2

Structure

2.1 Introduction

2.2 Objectives

2.3 Kinetic theory of gases

2.4 Mean free path

2.5 Transport Phenomena – Diffusion, Viscosity and Thermal conductivity

2.6 Maxwell's law of distribution of molecular velocities with experimental verification

2.7 Expression for mean velocity, mean square velocity and most probable velocity

2.8 Degrees of freedom and Law of equipartition energy

2.9 Liquefaction of gases

2.10 Liquefaction of air by Linde's method

2.11 Properties of Helium I & Helium II

2.12 Adiabatic demagnetization

2.13 Let us sum up

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2.15 Problems for discussion

2.16 Answers to check your progress

2.17 Suggested readings

2.1 Introduction

The experiments on the conversion of work into heat have shown clearly that heat is a form of energy. This energy is connected with the motion of molecules of which the matter is made of. Kinetic theory of matter (Solid, Liquid or Gas) gives an explanation to the nature of this motion and nature of heat energy. The kinetic theory of matter is based on three points (i) matter is made up of molecules (ii) molecules are in rapid motion and (iii) molecules experience forces of attraction between one another.

In the kinetic theory of gases, it is assumed that the molecules of gas are all identical and perfectly elastic spheres of negligible but finite size. Due to haphazard motion, the molecules constantly collide on each other. When the gas is not in equilibrium the random motion of gas molecules gives rise to viscosity, conductivity and diffusion, when it tries to attain an equilibrium state by transporting momentum, heat and mass respectively.

It was believed since ancient time that nothing could be colder than ice and hence temperature of ice was considered as zero (or starting point) of the scale. Moreover it was also thought that air remains in the gaseous state permanently at all temperatures. Later on Andrew's experiments on CO₂ gas in 1862 showed that

below the critical temperature, a gas can be liquefied by mere application of pressure. The lowest conceivable temperature on centigrade scale is -273°C much below the temperature of ice (0°C) and -273°C is universally taken as the zero of the absolute temperature scale, known as absolute zero temperature. Different methods are employed to reach the absolute zero temperature.

2.2 Objectives

After completing this unit you will be able to

- state the assumptions of kinetic theory of gases
- derive an expression for mean free path
- derive the expression for transport phenomena – diffusion, viscosity and thermal conductivity
- explain Maxwell's law of distribution of molecular velocities with experimental verification
- write the expression for mean velocity, mean square velocity and most probable velocity
- define degrees of freedom and law of equipartition energy
- describe the liquefaction of gases and explain the properties of Helium I & Helium II
- explain the principle of adiabatic demagnetization

2.3 Kinetic theory of gases

The kinetic energy of gases relates the macroscopic properties of gases (for example, pressure and temperature) to the microscopic properties of the gas molecule (for example, speeds and kinetic energies).

Postulates of the Kinetic Theory of Gases

1. A gas is composed of a large number of tiny, perfectly elastic particles, called molecules.
2. The molecules of a gas are identical in all respects.
3. The molecules of a gas are in a state of continuous motion. They move in all directions with all possible velocities. In their motion, they collide with each other and with the walls of the containing vessel. Collisions between molecules are elastic.
4. The molecules move in straight lines between any two consecutive collisions.
5. The average distance travelled by a molecule between two successive collisions is called the mean free path.
6. The time of impact is negligible in comparison to the time taken to traverse the free path.
7. The molecules do not exert any force of attraction or repulsion on one another.

8. The volume of the molecule is negligible, compared with the volume of the gas.
9. The molecules are perfectly hard elastic spheres and the whole of their energy is kinetic.

Check your progress

1. Explain and basics of kinetic theory, why upper atmosphere is cooled, while its kinetic temperature is of the order of 1000 K.

Ans: -----

2.4 Mean free path

Definition

The mean free path is defined as the average distance travelled by a molecule between two successive collisions.

Explanation

The molecules of a gas move about at random colliding with each other. Thus a molecule starting from A moves along AB and suffers a collision at B with another molecule. The magnitude and direction of the velocity of the molecule are changed and it moves along BC [Fig. 2.1]. After travelling a distance BC, it again suffers a collision at C and moves along CD and So on. AB, BC, CD, DE are all known as free paths and their individual lengths vary widely. The average of the free paths is called the mean free path.

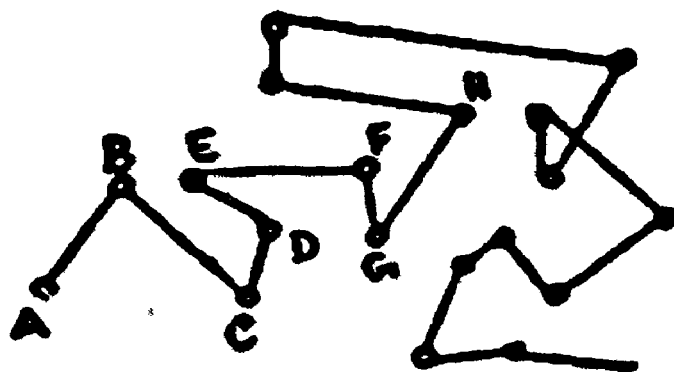


Fig. 2.1.

Let S be the total distance travelled in N collisions.

Then, the mean free path λ is given by

$$\lambda = \frac{S}{N}$$

Expression for Mean Free Path

Let us assume that only the particular molecule that we are considering in motion and all the other molecules are at rest. Let d be the diameter of one molecule. A collision between two molecules occurs if the distance between the centres of the two molecules is d [Fig. 2.2]. Consider one molecule moving with

the velocity v . In one second the molecule travels a distance v . Then the molecule will impinge on all static molecules in a cylinder of radius d and length v .

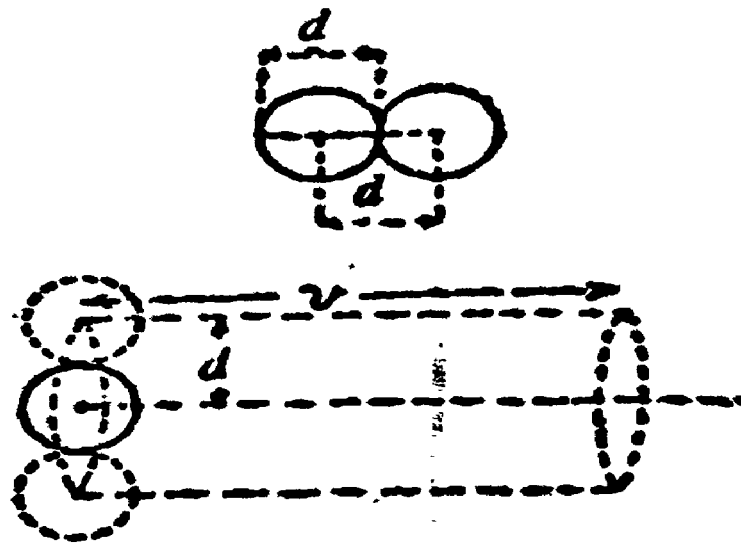


Fig.2.2

$$\text{Volume of the cylinder} = \pi d^2 v$$

$$\text{Number of molecules in this volume} = \pi d^2 v n$$

Here, n = number of molecules per unit volume.

Mean free path = λ

$$= \frac{\text{Total distance travelled by a molecule in 1 sec}}{\text{Total number of collisions per second}}$$

$$\lambda = \frac{v}{\pi d^2 v n} = \frac{1}{\pi d^2 n} \quad (1)$$

Maxwell showed that

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 n} \quad (2)$$

Let m be the mass of each molecule. Then $mn = \rho$ and $n = (\rho/m)$.

$$\lambda = \frac{m}{\sqrt{2} \pi d^2 \rho}$$

Thus the mean free Path is inversely proportional to the density of the gas.

Check your progress

2. Define mean free path.
3. The diameter of the nitrogen molecule is 3.2×10^{-10} m. The number of molecules at 0°C and 1 atm. pressure is 2.69×10^{25} per m^3 . Calculate the mean free path of nitrogen molecule.
4. Calculate the molecular diameter of nitrogen molecules if $n = 2.7 \times 10^{25}$ molecules per m^3 and mean free path λ for nitrogen is 8×10^{-8} m.

Ans: -----

2.5 Transport Phenomena – Diffusion, Viscosity and Thermal conductivity

Introduction

Viscosity of gases, thermal conductivity of gases and diffusion are called transport phenomena. They transport momentum, heat energy and mass, respectively from one layer of the gas to another.

2.5.1 Expression for the Coefficient of Diffusion

The coefficient of diffusion (D) is defined as the “the number of molecules diffusing per second per unit area per unit concentration gradient”.

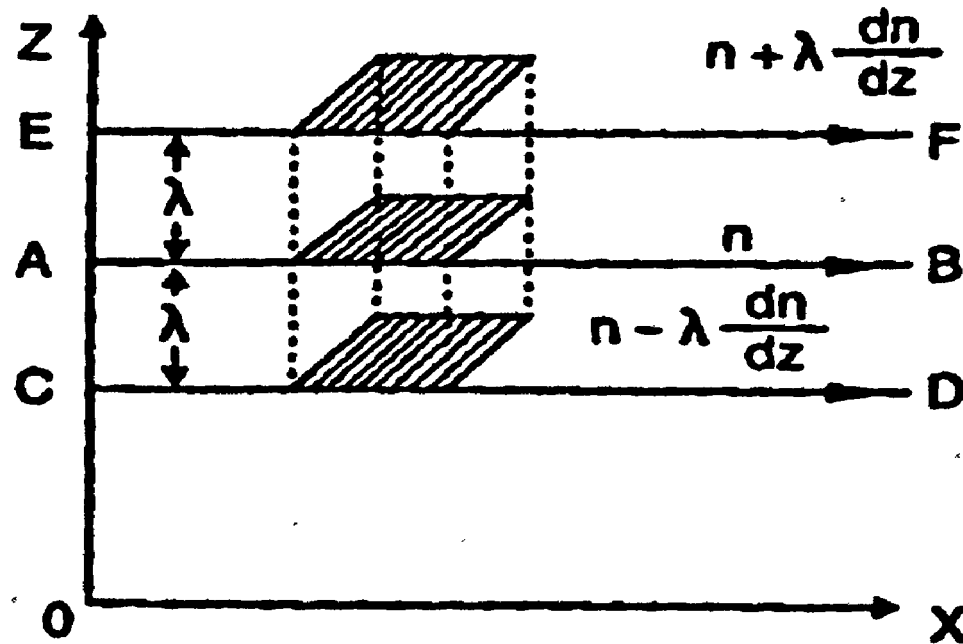


Fig. 2.3.

Consider that a mass of the gas is moving between the parallel planes CD and EF [Fig. 2.3]. The concentrations (number of molecules per unit volume) increases in vertical direction as we go from CD to EF. AB is an intermediate plane. In order to bring the equilibrium, the molecules of the gas will cross the plane AB from CD to EF vice versa, and due to thermal agitation.

Let, n = concentration of gas molecules of plane AB

$$\frac{dn}{dz} = \text{concentration gradient}$$

λ = distance between planes AB and EF
= mean free path

$$\text{Then, concentration at plane EF} = n + \lambda \left(\frac{dn}{dz} \right)$$

$$\text{Concentration at plane CD} = n - \lambda \left(\frac{dn}{dz} \right)$$

The molecules are moving in all possible directions. So $1/6$ of the total number of molecules are moving upward and equal number of molecules downward.

C is the r.m.s velocity of the molecules.

The number of molecules crossing plane AB downwards per unit area per second
 $= \frac{1}{6} C \left(n + \lambda \frac{dn}{dz} \right)$

The number of molecules crossing plane AB upwards per unit area per second
 $= \frac{1}{6} C \left(n - \lambda \frac{dn}{dz} \right)$

The net number of molecules crossing unit area of plane AB per second in

Downward direction $= \frac{1}{6} C \left(n + \lambda \frac{dn}{dz} \right) - \frac{1}{6} C \left(n - \lambda \frac{dn}{dz} \right) = \frac{1}{3} C \lambda \frac{dn}{dz}$

The coefficient of diffusion (D) is defined as the “the number of molecules diffusing per second per unit area per unit concentration gradient”.

$$D = \frac{\text{Number of molecules crossing unit area per second}}{\text{Concentration gradient}}$$

$$= \frac{\frac{1}{3} C \lambda \frac{dn}{dz}}{\frac{dn}{dz}}$$

$$D = \frac{1}{3} C \lambda$$

2.5.2 Expression for the Coefficient of Viscosity

The coefficient of viscosity of a gas (η) is defined as the “tangential force per unit area required to maintain a unit velocity gradient”.

Consider a gas flowing from left to right along a horizontal surface. Let the velocity of flow of the gas increase in the upward direction of the Z-axis. Let dv/dz be the velocity gradient along the Z-axis [Fig. 2.4].

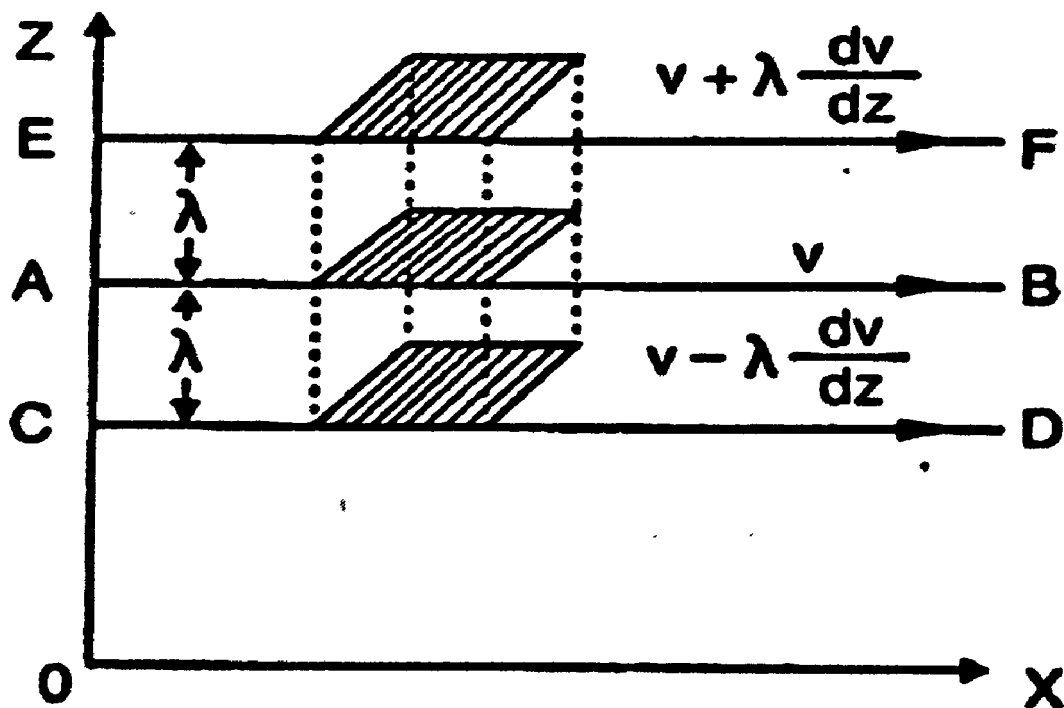


Fig.2.4.

Consider a layer AB moving with a velocity v . Now consider two layers EF and CD one above and other below AB, each at a distance λ (mean free path) from it.

$$\text{Velocity of flow of gas in the layer EF} = v + \lambda \left(\frac{dv}{dz} \right)$$

$$\text{Velocity of flow of gas in the layer CD} = v - \lambda \left(\frac{dv}{dz} \right)$$

Let m be the mass of each molecule.

$$\text{Momentum of each molecule in the layer EF} = m \left(v + \lambda \frac{dv}{dz} \right)$$

$$\text{Momentum of each molecule in the layer CD} = m \left(v - \lambda \frac{dv}{dz} \right)$$

Let n be the number of molecules per unit volume. Then $n/6$ molecules move parallel to any one axis in one particular direction. C is the r.m.s velocity of the molecules.

Number of molecules crossing unit area of AB downwards in one second

$$= \frac{n}{6} C$$

The momentum carried downward by the molecules crossing unit area of AB per second from the plane EF

$$= \frac{mnC}{6} \left(v + \lambda \frac{dv}{dz} \right)$$

Similarly, the momentum carried upwards

$$= \frac{mnC}{6} \left(v - \lambda \frac{dv}{dz} \right)$$

Net momentum transferred per unit area per second downwards

$$= \frac{mnC}{6} \left(v + \lambda \frac{dv}{dz} \right) - \frac{mnC}{6} \left(v - \lambda \frac{dv}{dz} \right) = \frac{1}{3} mnC \lambda \frac{dv}{dz}$$

This is equal to the tangential viscous force acting per unit area of the layer AB.

The coefficient of viscosity,

$$\eta = \frac{\text{tangential force}}{\text{velocity gradient}}$$

$$= \frac{\frac{1}{3} mnC \lambda \frac{dv}{dz}}{\frac{dv}{dz}} = \frac{1}{3} mnC \lambda$$

$mn = \rho$ (density of the gas)

$$\eta = \frac{1}{3} \rho C \lambda$$

1.5.3 Expression for the Coefficient thermal Conductivity

The coefficient of thermal conductivity of a gas (K) of a gas is defined as the “quantity of heat flowing per unit area per unit time per unit temperature gradient.

Consider three layers CD, AB and EF of the gas [Fig. 2.5]. Let θ be the temperature of the gas in the plane AB. The temperature increases as we go from the plane CD to EF. Let $d\theta/dz$ be the temperature gradient along the z-axis. Let each of the layers CD and EF be at a distance λ from AB. λ is the mean free path

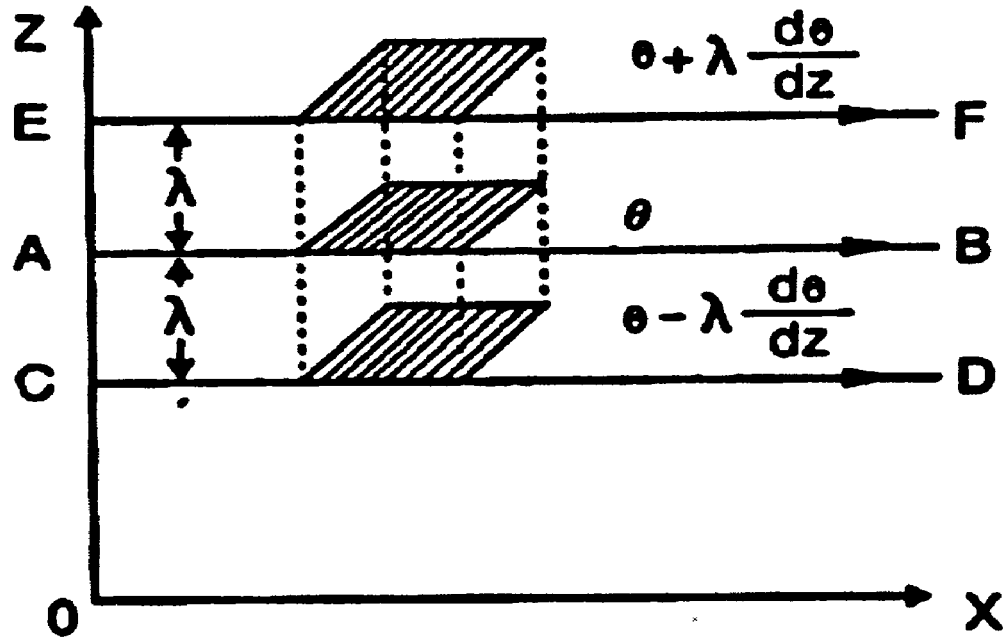


Fig. 2.5.

Temperature of the molecules in the layer EF = $\theta + \lambda \left(\frac{d\theta}{dz} \right)$

Temperature of the molecules in the layer CD = $\theta - \lambda \left(\frac{d\theta}{dz} \right)$

Due to the random motion of the molecules, there will be a continual interchange of molecules between layers CD and EF.

Let m = mass of each molecule,

C = r.m.s velocity of the molecules,

n = number of molecules per unit volume.

Number of molecules crossing the plane AB upwards or downwards per unit area per second = $\frac{n}{6}c$

Heat carried by molecules from EF, crossing unit area of AB downwards per second = $\frac{mnC}{6} C_v \left(\theta + \lambda \frac{d\theta}{dz} \right)$

Here, C_v = Specific heat capacity of the gas at constant volume.

Heat carried by molecules from CD, crossing unit area of AB upwards per second = $\frac{mnC}{6} C_v \left(\theta - \lambda \frac{d\theta}{dz} \right)$

Therefore, net amount of heat transferred per unit area of AB per second = Q

$$= \frac{mnC}{6} C_v \left(\theta + \lambda \frac{d\theta}{dz} \right) - \frac{mnC}{6} C_v \left(\theta - \lambda \frac{d\theta}{dz} \right) = \frac{1}{3} mnCC_v \left(\lambda \frac{d\theta}{dz} \right)$$

$$K = \frac{\frac{1}{3} mnCC_v \lambda \frac{d\theta}{dz}}{\frac{d\theta}{dz}} = \frac{1}{3} \rho CC_v \lambda$$

The coefficient of thermal conductivity of a gas (K) of a gas is defined as the “quantity of heat flowing per unit area per unit time per unit temperature gradient.

$$K = \frac{\frac{1}{3} mnCC_v \lambda \frac{d\theta}{dz}}{\frac{d\theta}{dz}} = \frac{1}{3} \rho CC_v \lambda$$

$$K = \frac{1}{3} \rho CC_v \lambda$$

Check your progress

5. Define the coefficient of Diffusivity.

6. Viscosity of oxygen at 27°C is $2 \times 10^{-5} \text{Ns/m}^2$. Calculate the diameter of the oxygen molecules.

Ans: -----

2.6 Maxwell’s law of distribution of molecular velocities with experimental verification

A gas contains a very large number of molecules. These molecules have incessantly and haphazardly in all possible directions with all possible velocities ranging from $-\infty$ to ∞ . Maxwell derived an expression for the number of molecules lying between a given velocity range c and $c +dc$. Such a law is known as velocity distribution law.

Let dN be the number of molecules with velocities between c and $c +dc$.

Then

$$dN = 4\pi N A^3 e^{-mc^2/2kT} C^2 dc \quad (1)$$

Here, N is the number of molecules per unit volume.

$$A = \sqrt{m / (2\pi kT)}$$

m = Mass of a molecule.

k = Boltzmann constant and T is the absolute temperature of the gas.

This is the equation for the Maxwell's law of distribution of molecular speeds in a gas.

The graph representing dN/dc and speed c is shown in Fig.2.6.

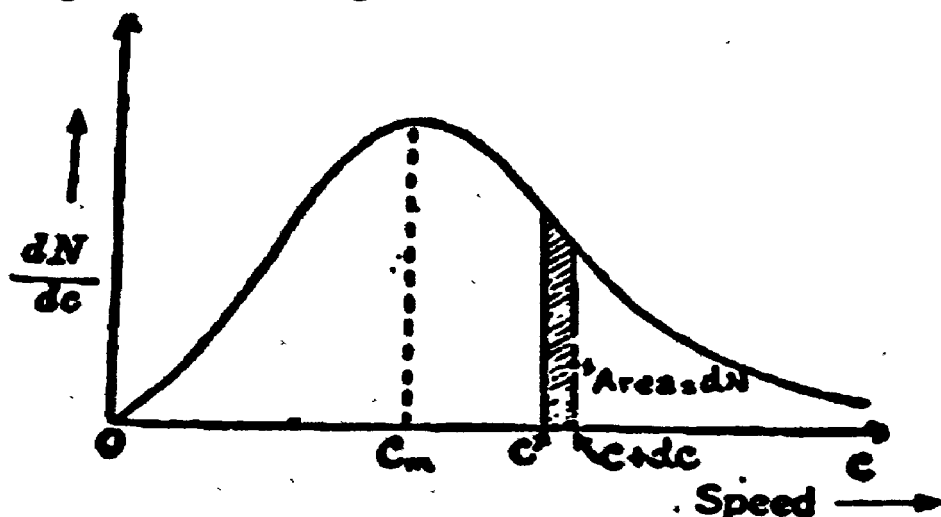


Fig.2.6.

- i. The shaded area in the figure represents the number of molecules dN having velocities between c and $c+dc$.
- ii. The total area under the curve represents the total number of molecules.
- iii. The number of molecules having very low or very high velocity is small.
- iv. The maximum corresponds to the most probable speed (c_m).

The most probable speed is the speed possessed by maximum number of molecules in a gas.

Experimental verification-Lammert's toothed wheel method

The experimental arrangement is shown in fig.2.7. W_1 and W_2 are two equal toothed wheels, with 50 teeth each and 50 narrow slits in between them.

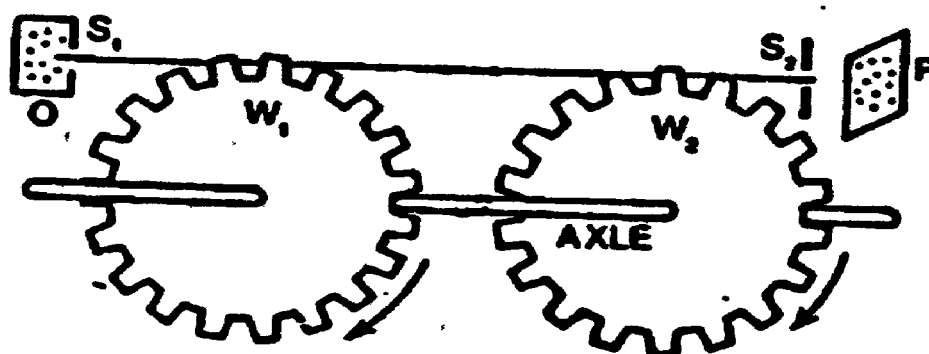


Fig. 2.7.

They are mounted on the same axle. The slits in W_2 are not parallel to those in W_1 but are displaced at an angle of 2° behind them. An oven O contains mercury vapor which comes out of a slit S_1 . S_2 is another similar and parallel slit.

The wheels are set in rapid rotation. Mercury is then heated in the oven. The mercury beam passing through slit S_1 falls on the slot in W_1 . The molecules passing through the slot of W_1 now fall on wheel W_2 . The principle of the experiment is based on the fact that those molecules are able to pass through a slot in W_2 which have the requisite speed to cover the distance W_1W_2 in the small

interval of time taken by the wheel to turn through an angle of 2° . These molecules are deposited on the plate P. Thus the molecules having a particular speed can be separated from the rest.

By rotating the wheels with various speeds, the molecules of different speeds are collected at different places on the plate P. The relative intensities in each case are measured by a micro photometer. From this measurement, the relative numbers of molecules lying in different velocity ranges are calculated. It is found that the distribution of speeds agrees with Maxwell's distribution law.

2.7 Expression for mean velocity, mean square velocity and most probable velocity

Mean velocity is the average velocity of all the molecules.

$$\langle c \rangle = \frac{1}{N} \int_0^\infty c dN = \sqrt{\frac{8kT}{\pi m}}$$

Mean square velocity is the average of the squares velocities of all the molecules.

$$\langle c^2 \rangle = \frac{1}{N} \int_0^\infty c^2 dN = \frac{3kT}{m}$$

Most probable velocity is that velocity c for which the number of molecules with that velocity is the maximum.

$$c_m = \sqrt{\frac{2kT}{m}}$$

Thus $c_m^2 : \langle c \rangle^2 : \langle c^2 \rangle = 1 : 1.27 : 1.5$.

Check your progress

7. Write the equation for Mean square velocity.

8. Calculate the rms velocity of hydrogen at 27°C . $k = 1.38 \times 10^{-23} \text{ J/K}$ and mass of hydrogen molecule = $3.34 \times 10^{-27} \text{ Kg}$. Also find the most probable speed.

Ans: -----

2.8 Degrees of freedom and Law of equipartition energy

Definition:

The degrees of the freedom of a dynamical system may be defined as the total number of independent coordinates required to specify completely its position and configuration.

Explanation:

The position of an ideal mass point in space can be defined completely by the three Cartesian coordinates x , y , z . Hence, it has three degrees of freedom. Two points will require at least six coordinates to define their positions in space. Hence they have six degrees of freedom.

(i) Monatomic gas molecule.

A mono-atomic molecule (Helium, Neon, Argon *etc.*.) consists of one single atom. It has three degrees of freedom of translational motion along the three coordinate axes. (Fig.2.8).

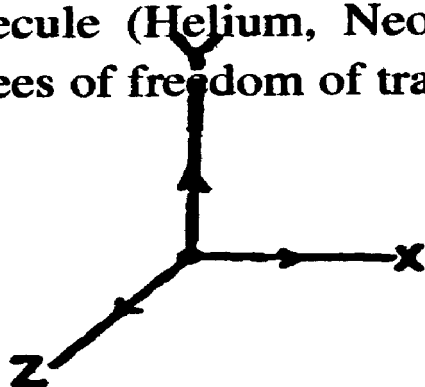


Fig.2.8

(ii) Diatomic gas molecule.

A diatomic gas molecule (H_2 , O_2 , N_2 , CO *etc.*.) has two atoms at a fixed distance apart.

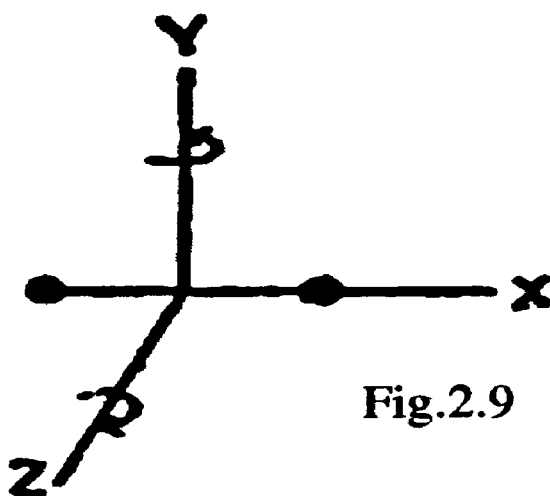


Fig.2.9

It has three degrees of freedom of translational motion and two of rotational motion (Fig.2.9). Hence, a diatomic molecule has five degrees of freedom.

2.8.2 Equipartition of energy

Statement:

For any dynamical system in thermal equilibrium, the total energy is divided equally among all the degrees of freedom. The energy associated with one

molecule per degree of freedom = $\frac{1}{2}kT$ = constant.

Here, k = Boltzmann's constant.

T = absolute temperature of the thermo dynamical system.

Now, one mole of a gas contains N molecules.

The average kinetic energy associated with each degree of freedom

$$= \frac{1}{2}kT \times N = \frac{1}{2}RT$$

Here, N = Avogadro number,

R = gas constant for one mole of the gas.

This principle is true for all degrees of freedom, translational, rotational or vibrational.

Explanation:

The mean kinetic energy of translation of a mono-atomic gas molecule at a temperature T is given by

$$\frac{1}{2}mC^2 = \frac{3}{2}kT$$

$$\text{But } C^2 = u^2 + v^2 + w^2$$

Mean square velocities along the three axes are equal. Here, u,v,w are the components of C along the X, Y, and Z axes respectively.

$$u^2 = v^2 = w^2$$

$$\text{or } \frac{1}{2}mu^2 = \frac{1}{2}mv^2 = \frac{1}{2}mw^2$$

$$\frac{1}{2}mC^2 = 3 \left[\frac{1}{2}mu^2 \right] = 3 \left[\frac{1}{2}mv^2 \right] = 3 \left[\frac{1}{2}mw^2 \right] = \frac{3}{2}kT$$

$$\left[\frac{1}{2}mu^2 \right] = \frac{1}{2}kT$$

$$\left[\frac{1}{2}mv^2 \right] = \frac{1}{2}kT$$

$$\left[\frac{1}{2}mw^2 \right] = \frac{1}{2}kT$$

Therefore, the average kinetic energy associated with each degree of freedom

$$= \frac{1}{2}kT$$

2.9 Liquefaction of gases

A gas goes into liquid and solid forms as the temperature is reduced. Thus the process of liquefaction of gases and solidification of liquids are intimately involved in the production of low temperatures. Andrews's experiments showed that if a gas is to be liquefied by merely applying pressure on it, it has to be cooled below its critical temperature. Critical temperatures of CO₂, NH₃ and SO₂ are higher than room temperature. Hence these gases can be liquefied at room temperature without pre-cooling, simply by increasing the pressure. So, the simple

process would be to cool the gas below its critical temperature by some coolant and then to liquefy it by applying pressure on it. This method does not work always. In the case of some gases like oxygen, nitrogen, hydrogen and helium, no precooling can bring the temperature below their critical temperatures. Thus they cannot be liquefied by this method.

Joule – Thomson expansion is a very important technique to liquefy gases. The cooling produced in J-T expansion of a gas depends on the difference of pressure on the two sides of the porous plug and the initial temperature. For most of the gases, the J-T cooling is very small. However, the cooling effect can be intensified by employing the process called regenerative cooling.

2.10 Liquefaction of air by Linde's method

Linde liquefied air using Joule – Thomson effect and the principle of regenerative cooling.

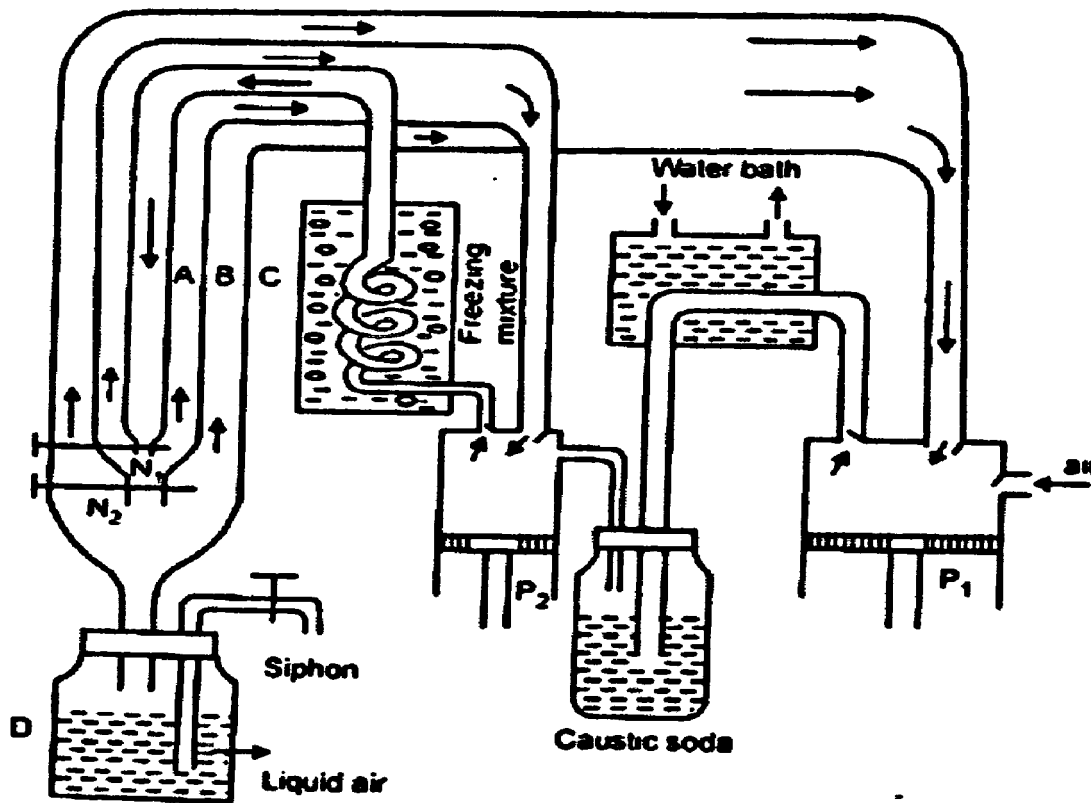


Fig.2.10.

The apparatus used is shown in Fig. 2.10. Air is compressed to a pressure of about 25 atmospheres by the pump P_1 . It is then cooled by passing it through the cold water bath. This compressed air is passed through KOH solution to remove CO_2 and water vapor. The air then enters the second pump P_2 . Here it is compressed to a pressure of about 200 atmospheres. The compressed air next passes through a cooling spiral immersed in a freezing mixture, where its temperature falls to about -20°C . This cooled air at high pressure passes down through the tube A and is allowed to come out of the nozzle N_1 . The temperature falls to about -70°C . This cooled air flows upwards through the tube B, cools the incoming air through A and returns to P_2 . The pump P_2 again compresses the air to

200 atmospheres and puts it into circulation once more. It passes through the nozzle N_1 and is further cooled.

After the completion of a few cycles, the air is cooled to a sufficiently low temperature. At this stage, the second nozzle N_2 is opened. The already much cooled air is allowed to expand to a pressure of one atmosphere when it is liquefied. The liquid air is collected in a Dewar flask D. The unliquefied air is led back through the tube C to the pump P_1 and the process is repeated. The entire arrangement is packed in cotton wool to avoid any conduction or radiation.

2.11 Properties of Helium I & Helium II

2.11.1 Liquid Helium I and II

- i. Kamerlingh Onnes found a specific discontinuity in the density of helium at 2.19 K. This is shown in Fig.2.11. The density of liquid helium increases as the temperature decreases from 4 K to 2.19 K. The density becomes maximum (146.2 kg/m^3) at 2.19 K. Then the density decreases with decrease of temperature. Thus, liquid helium which is contracting when cooled suddenly begins to expand below 2.19 K. At 2.19 K, a sudden discontinuity appears in density versus temperature curve.

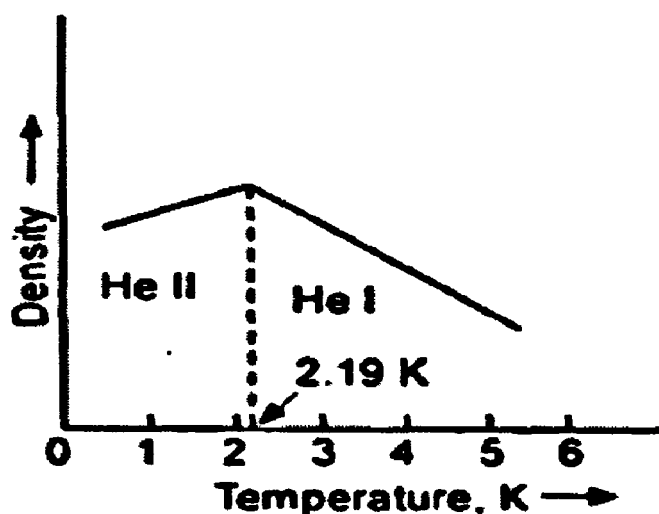


Fig.2.11

- ii. Later Keesom also found another specific discontinuity at 2.19 K. He measured the specific heat capacity of helium at different temperatures. The result is shown in Fig.2.12.

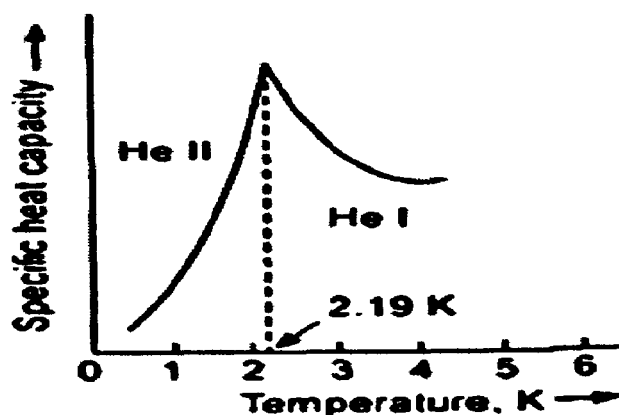


Fig.2.12

- iii. As helium is gradually cooled from 4.2 K, the specific heat capacity remains approximately constant at first and near 2.19 K it increases a little. Exactly at 2.19 K, specific heat capacity increases suddenly to a very large value. Then it gradually falls as the temperature is reduced from 2.19 K. The graph resembles the Greek letter λ . Hence this temperature (2.19 K) at which specific heat capacity changes abruptly is called the λ – point. The properties of liquid helium above and below λ – point are quite different. Liquid helium above 2.19 K is called helium I and it behaves in a normal manner. Liquid helium below 2.19 K is called helium II because of its abnormal properties.
- iv. Kessom later found a similar discontinuity in the dielectric constant also of this liquid at λ – point.
- v. The coefficient of viscosity of liquids, in general, increases with decrease in temperature. But the viscosity of liquid helium I decreases with increase in temperature. Further, the viscosity of liquid helium II is almost zero and it can flow rapidly through narrow capillary tubes. Its rate of flow does not depend upon the pressure difference between the ends of the capillary tube. Hence it is called a super fluid. This property is called super fluidity.

2.11.2 Properties of Helium II

- i. **Density:** The densities of helium I and II are about the same in the neighborhood of 0.146 kg/m^{-3} which is far less than the lightest of other liquids.
- ii. **Extreme fluidity:** He II has practically zero viscosity and is called a super fluid. Its rate of flow through tubes is quite independent of the pressure difference across them.
- iii. **High heat conductivity:** He II has an extraordinarily high coefficient of thermal conductivity. He II is said to be about 800 times more conducting than copper.
- iv. **Formation of films over solid surfaces:** In order to explain the extraordinary fluidity and thermal conductivity of He II, Rollin and Simon suggested that it may be due to the formation of a creeping film of it over the solid surfaces in contact with it. This film is called the Rollin Simon film and is about 100 atomic layers or about $5 \times 10^{-8} \text{ m}$ thick. If a test tube containing liquid He II is placed in a Dewar flask containing liquid He II, the following creeping actions are observed:
 - a) If the level of liquid in the test tube is lower than the level in the flask, the liquid from outside starts creeping into the tube along its outer walls (Fig. 2.13). This process continues till the levels inside and outside the tube is equalized.

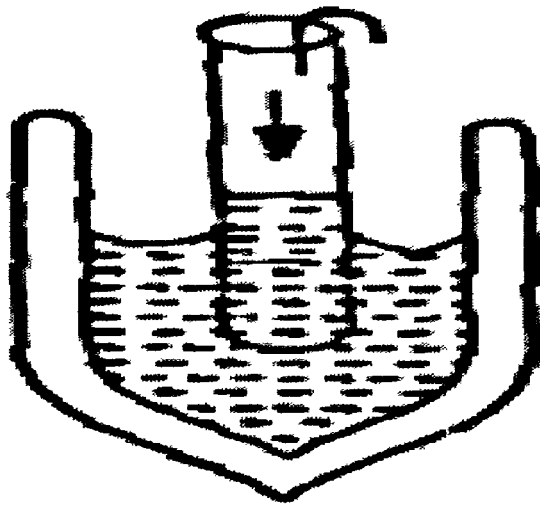


Fig.2.13

- b) Suppose the tube is raised up so that the level of helium inside the tube is higher than that outside it. Then the liquid from inside the tube starts creeping out of it along its inner walls till the two levels are equalized (Fig. 2.14).

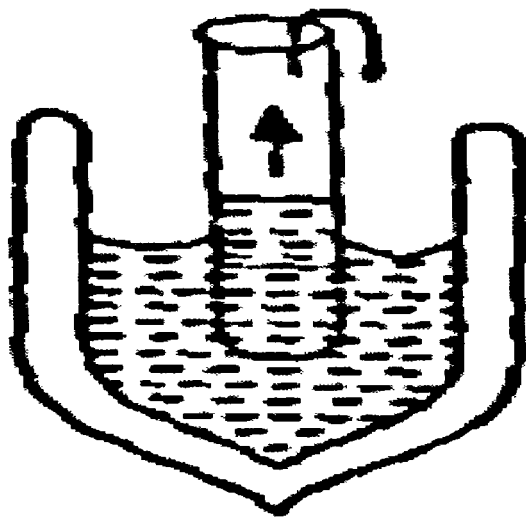


Fig.2.14

- c) Suppose the tube is raised above the level of liquid in the flask, the liquid inside the tube now creeps out along the surface of the tube, collects at its bottom in the form of drops and falls in to the liquid below. This continues until the entire liquid inside the tube is drained out (Fig. 2.15).

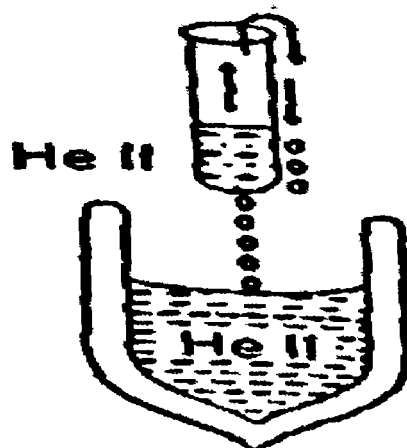


Fig.2.15

- v) **The Fountain Effect:** Helium II is taken in a tube AB (Fig. 2.16.). The upper part A of a tube is in the form of capillary. The lower part B of the tube is packed with fine emery powder (with inter-spaces between the grains of the order of a micron) and with a small hole O at the bottom. The tube is placed inside a Dewar flask containing He II.

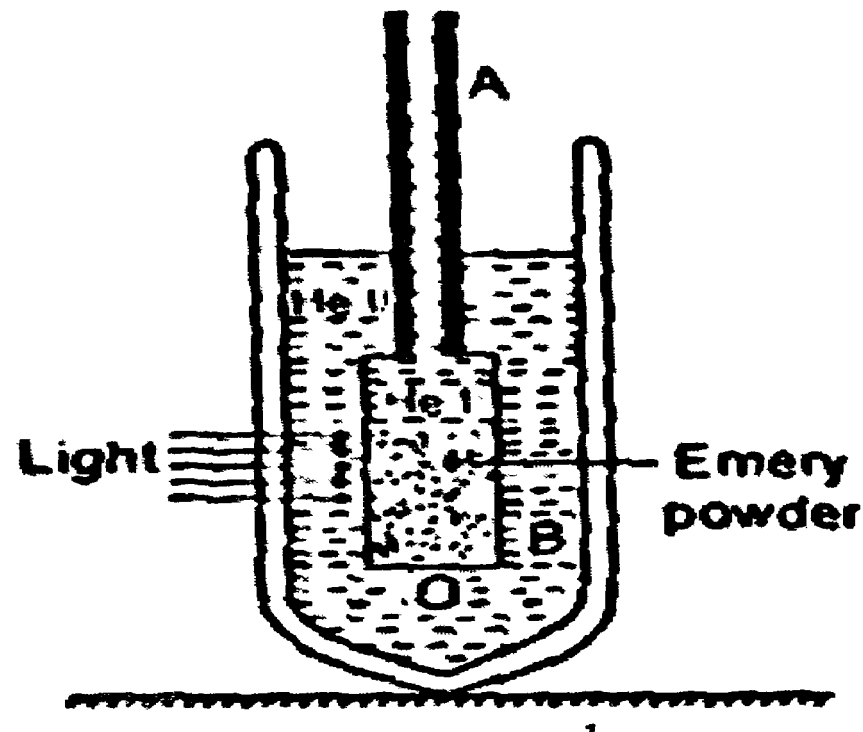


Fig 2.16

On throwing a flash of light on the powder from an ordinary torch, part of He II is found to spur out of the capillary tube in the form of fountain. This shows that the liquid develops a pressure in a direction opposite to that of the temperature gradient created by shining light on the powder.

2.12 Adiabatic demagnetization

Principle:

When a paramagnetic substance is magnetized, external work is done on it and its temperature rises. When the substance is demagnetized, work is done by the substance. Hence, if the substance is demagnetized adiabatically, its temperature falls. This is called magneto caloric effect.

Maximum cooling can be produced by employing strong magnetic field and low initial temperature.

Curie's law:

According to Curie law, the paramagnetic susceptibility χ of a substance is inversely proportional to the absolute temperature T, i.e.,

$$\chi \propto \frac{1}{T}$$

$$\text{(Or) } \chi = \frac{c}{T} \text{ Here, } c \text{ is a constant.}$$

Thus, the susceptibility of a paramagnetic substance is higher, the lower the temperature is. Hence, a paramagnetic substance is powerfully magnetized at

very low temperature. When this substance is adiabatically demagnetized, a large cooling is produced.

Giauque's method:

The experimental arrangement is shown in Fig. 2.17.

The paramagnetic salt (gadolinium sulphate) is suspended inside a glass bulb B. Bulb B is surrounded by Dewar flask D₁ and D₂ containing liquid helium and liquid hydrogen respectively. The whole arrangement is placed between the poles of a strong electromagnet.

- i. The magnetic field is switched on, so that the specimen is magnetized.
- ii. The heat due to magnetization is removed by first introducing hydrogen gas into B and then pumping it off with a high vacuum pump. Now the cold magnetized specimen is thermally isolated from D₁ and D₂.
- iii. The magnetic field is now switched off.

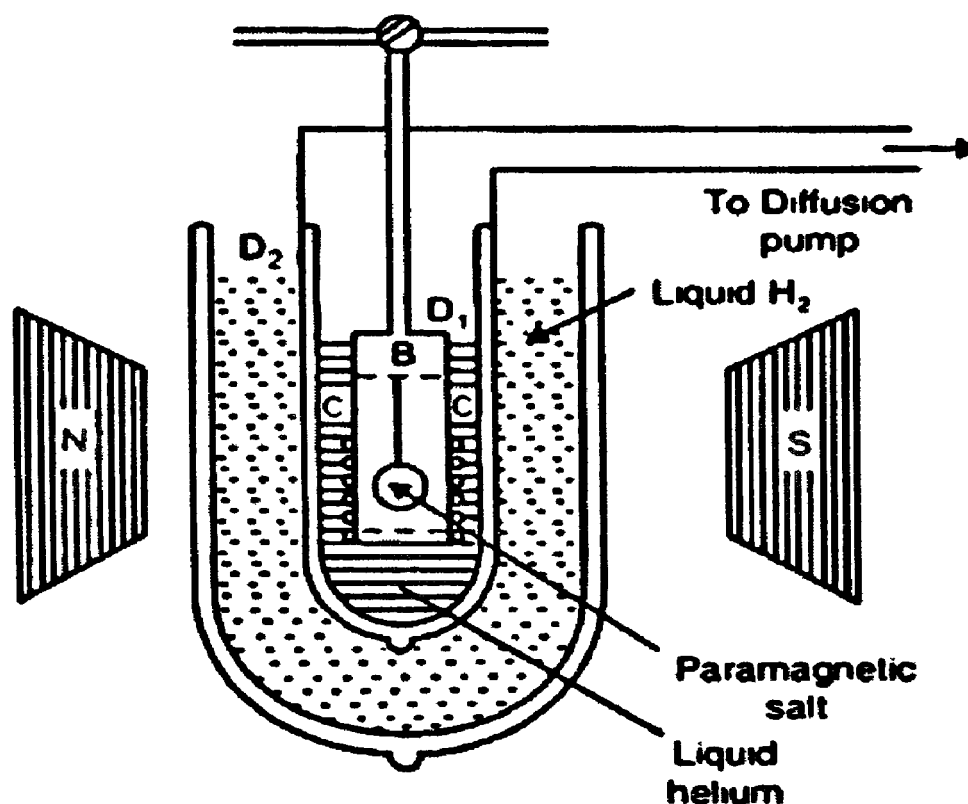


Fig.2.17

Adiabatic demagnetization of the specimen takes place and its temperature falls. The final temperature of the specimen (T_2) is determined by measuring the susceptibility of the substance at the beginning and at the end of the experiment by using a solenoid coil CC.

Let χ_1 and χ_2 be the susceptibilities of the specimen salt at the initial and final temperature T_1 and T_2 . Then, according to Curie's law,

$$\frac{\chi_1}{\chi_2} = \frac{T_2}{T_1}$$

Or
$$T_2 = \frac{\chi_1}{\chi_2} T_1$$

Using this method with the salt gadolinium sulphate, Giauque and MacDougall reached a temperature of 0.25 K.

2.13 Let us sum up

- Kinetic theory is based on two postulates: matter is made up of molecules which are in a state of constant random motion.
- The mean free path is defined as the average distance travelled by a molecule between two successive collisions and is given by $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$
- The Coefficient of Diffusion D for gases is $= \frac{1}{3} C \lambda$
- The Coefficient of viscosity for gases is $\eta = \frac{1}{3} \rho C \lambda$
- The Coefficient of Thermal conductivity for gases is $K = \frac{1}{3} \rho C C_v \lambda$
- Maxwell's law of distribution of molecular velocities

$$dN = 4\pi N A^3 e^{-mc^2/2kT} C^2 dc$$
- Expression for Mean velocity is $\langle c \rangle = \sqrt{\frac{8kT}{\pi m}}$
- Expression Mean square velocity $\langle c^2 \rangle = \frac{3kT}{m}$
- Expression Most probable velocity $c_m = \sqrt{\frac{2kT}{m}}$
- The degrees of the freedom of a dynamical system may be defined as the total number of independent coordinates required to specify completely its position and configuration.
- For any dynamical system in thermal equilibrium, the total energy is divided equally among all the degrees of freedom are the law of equipartition Energy.
- Gases can be liquefied below a critical temperature by application of Pressure and regenerative cooling.
- Peculiar properties of Helium II are super fluidity, high heat conductivity, and high electrical conductivity, formation of rolling film, the fountain effect and Mechanocaloric effect.
- When a paramagnetic substance is magnetized, external work is done on it and its temperature rises. When the substance is demagnetized, work is done by the substance. Hence, if the substance is demagnetized adiabatically, its temperature falls. This is called magneto caloric effect.

2.14 Unit – end exercises

1. State the postulates of kinetic theory of gases.
2. Define mean free path. Derive an expression for it.
3. Using transport phenomena, Explain (i) the diffusion (ii) viscosity and (iii) thermal conductivity of gases
4. Discuss the Maxwell's law of distribution of molecular speeds and describe the experimental verification.
5. What you mean by degrees of freedom and state the laws of equipartition energy.
6. Discuss the Linde's method of liquefaction of oxygen.
7. What are the properties of liquid Helium I and II?
8. What is adiabatic demagnetization? Describe the method of production of low temperature by adiabatic demagnetization of a paramagnetic salt.

2.15 Problems for discussion

1. Calculate the mean free path of the gas molecule, given that the molecular diameter is 2×10^{-8} cm and the number of molecules per cc is 3×10^{19} .
2. In an experiment, the viscosity of the gas was found to be 2.25×10^{-4} CGS units. The rms velocity of the molecule is 4.5×10^4 cm/second. The density of the gas is 1 gram / litre. Calculate the mean free path of the molecules.
3. Calculate the number of collisions per second of a molecule of a gas having mean free path 1.876×10^{-7} m. Take average speed of the molecule as 511 m/s
4. Calculate the (i) mean free path (ii) the number of collisions made per second and (iii) its molecular diameter of a nitrogen gas having the mean velocity of a molecule as 450 m/s. Density at N.T.P is 1.25 kg / m^3 , coefficient of viscosity is $16.6 \times 10^{-6} \text{ Ns/m}^2$ and $n = 2.7 \times 10^{23}$ per m^3 .
5. Calculate the temperature at which the rms velocity of a hydrogen molecule will be equal to the speed of the earth's first satellite $V = 8 \text{ Km/s}$.

2.16 Answers to check your progress & problems for discussion:

Check your progress:

1. The quantity of heat of an individual molecule in the upper atmosphere is increased about 3.5 times than that at the earth's surface. Kinetic temperature on earth surface is about 300 K, while in the upper atmosphere it is of the order of 1000 K. But the pressure and hence the density is very low in upper atmosphere i.e., the number of molecules per cc is very small, thus the total heat content in the upper atmosphere is very small as compared to the heat content on the earth in the same volume of gas.

2. The mean free path is defined as the average distance travelled by a molecule between two successive collisions and is given by $\lambda = \frac{1}{\sqrt{2}\pi d^2 n}$.

3. The mean free path λ is given by,

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} = \frac{1}{\sqrt{2} \times 3.14 \times (3.2 \times 10^{-10})^2 \times 2.69 \times 10^{25}}$$

$$= \frac{1}{122.32} \times 10^{-5} = 0.008175 \times 10^{-5} \text{ m}$$

4. The mean free path λ is given by,

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

$$\sigma^2 = \frac{1}{\sqrt{2}\pi\lambda n} = \frac{1}{\sqrt{2} \times 3.14 \times (8 \times 10^{-8}) \times 2.7 \times 10^{25}}$$

$$= \frac{1}{95.918} \times 10^{-17} = 0.03229 \times 10^{-8} \text{ m}$$

5. The coefficient of diffusion (D) is defined as the “the number of molecules diffusing per second per unit area per unit concentration gradient”.

6. We have viscosity,

$$\eta = \frac{1}{3} \rho \langle c \rangle \lambda$$

$$\text{But } \langle c \rangle = \sqrt{\frac{8kT}{m\pi}}$$

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

$$\eta = \frac{1}{3} mn \left(\sqrt{\frac{8kT}{m\pi}} \right) \left(\frac{1}{\sqrt{2}\pi\sigma^2 n} \right)$$

$$\sigma^2 = \frac{1}{3\pi\eta} \frac{\sqrt{4mkT}}{\pi}$$

$$\sigma = \frac{1}{[3\pi(2 \times 10^{-5})]^{1/2}} \left(\frac{[(4 \times 32) / (6.02 \times 10^{26})] (1.38 \times 10^{-23}) \times 300}{3.14} \right)^{1/4}$$

$$\sigma = 3.968 \times 10^{-8} \text{ m}$$

$$7. \quad \langle c^2 \rangle = \frac{1}{N} \int_0^{\infty} c^2 dN = \frac{3kT}{m}$$

8. Given T = 300 K

$$k = 1.38 \times 10^{-23} \text{ J / K m} = 3.34 \times 10^{-27} \text{ Kg}$$

$$C_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times (1.38 \times 10^{-23}) \times 300}{3.34 \times 10^{-27}}}$$

$$= 1928 \text{ m/s}$$

$$C_m = \sqrt{\frac{2}{3}} C_{rms} = \sqrt{\frac{2 \times 1928}{3}}$$

$$= 1574 \text{ m/s}$$

Answers to problems for discussion:

1. The mean free path λ is given by,

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n} = \frac{1}{\sqrt{2} \times 3.14 \times (2 \times 10^{-8})^2 \times 3 \times 10^{19}}$$

$$= 2.12 \times 10^{-5} \text{ cm} = 2.12 \times 10^{-7} \text{ m}$$

(The mean free path is less than the wavelength of light in the visible spectrum).

2. $\eta = 2.25 \times 10^{-4}$ CGS units, $C = 4.5 \times 10^4$ cm/s,

$$\rho = 1 \text{ g/litre} = 10^{-3} \text{ g/cc}$$

$$\lambda = \frac{3\eta}{\rho C} = \frac{3 \times 2.25 \times 10^{-4}}{10^{-3} \times 4.5 \times 10^4} = 15 \times 10^{-8} \text{ m}$$

3. Mean free path $\lambda = 1.876 \times 10^{-7} \text{ m}$, $v = 511 \text{ m/s}$

$$\text{Collision frequency } f = \frac{v}{\lambda} = \frac{511}{1.876 \times 10^{-7}} = 2.72 \times 10^9 \text{ per second}$$

4. (i) We have,

$$\eta = \frac{1}{3} \rho C \lambda$$

$$\lambda = \frac{3\eta}{\rho C} = \frac{3 \times 16.6 \times 10^{-6}}{1.25 \times 450} = 8.853 \times 10^{-8} \text{ m}$$

$$\text{(ii) Number of collisions per second} = \frac{C}{\lambda} = \frac{450}{8.853 \times 10^{-8}} = 5.083 \times 10^9$$

$$\text{(iii) } \lambda = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

$$\sigma^2 = \frac{1}{\sqrt{2}\pi\lambda n} = \frac{1}{\sqrt{2} \times 3.14 \times (8.853 \times 10^{-8}) \times 2.7 \times 10^{23}}$$

$$\sigma = 3.068 \times 10^{-10} \text{ m.}$$

3 Energy for 1 gm molecule of hydrogen

$$= \frac{1}{2} m v^2 = \frac{3}{2} R T$$

$$T = m v^2 / 3R = [2 \times (8 \times 10^5)^2] / [3 \times 8.3 \times 10^7]$$

$$T = 5140 \text{ K}$$

2.17 Suggested readings

- 1. Heat, Thermodynamics and Statistical Physics**
Brijlal, Dr. N. Subramanyam and P. S. Hemne.
Revised edition, Reprint 2012 S.Chand& Company Ltd., New Delhi
- 2. Thermodynamics and Statistical Physics**
Singhal, Agarwal, SathyaPrakash
12th edition, 2008, PragatiPrakashan, Meerut
- 3. Thermodynamics, Statistical thermodynamics and Kinetics**
Thomas Engal, Philip Reid
1st edition, 2007, Dorling Kindersley (India) Pvt Ltd, New Delhi.

UNIT 3

Structure

3.1 Introduction

3.2 Objectives

3.3 Thermal conductivity & thermal diffusivity

3.4 Rectilinear flow of heat - Ingen-Hausz experiment

3.5 Thermal conductivity of a bad conductor - Lee's method

3.6 Black body radiation - Wein's Law, Rayleigh - Jeans Law and Plank's Law

3.7 Stefan's law & Solar constant - Experimental verification

3.8 Let us sum up

3.9 Unit - End Exercises

3.10 Problems for discussion

3.11 Answers to Check your progress.

3.12 Suggested readings.

3.1 Introduction:

Heat can be transferred from one place to the other by three different ways *viz.* conduction, convection, and radiation.

Conduction is the process in which heat is transmitted from one point to the other through the substance without the actual motion of the particles. When one end of a metal bar is heated, the molecules at the hot end vibrate with higher amplitude (kinetic energy) and transmit the heat energy from one particle to the next and so on. However, the particles remain in their mean positions of equilibrium. This process of conduction is prominent in the case of solids. The property of transmission of heat has been used in Davy's safety lamp. Materials having less conductivity *e.g.* granite, brick walls etc. are used in the construction of a cold storages, furnace of a boiler etc. The space between the two walls of a thermos flask is evacuated because vacuum is a poor conductor of heat. The air enclosed in the woollen fabric helps in protecting us from cold, because air is a poor conductor of heat.

Convection is the process in which heat is transmitted from one place to the other by the actual movement of the heated particles. It is prominent in the case of liquids and gases. Land and sea breezes and trade winds are formed due to convection. Convection plays an important part in ventilation, gas filled electric lamps and heating of buildings by hot water circulation.

Radiation is the process in which heat is transmitted from one place to the other directly without the necessity of the inter-veining medium. We get heat radiations directly from the sun without affecting the intervening medium. Heat radiations can pass through vacuum. Their properties are similar to light radiations. Heat radiations also form a part of the electromagnetic spectrum.

3.2 Objectives:

After going through this unit, you will be able to:

- Define thermal conductivity, and thermal diffusivity
- Obtain an expression for the thermal conductivity of a bad conductor
- Explain the concept of black body radiation
- Define Stefan's constant, solar constant and its experimental verification

3.3 Coefficient of Thermal Conductivity

Consider a cube of side x cm and area of each face A sq cm. The opposite faces of the cube are maintained at temperatures.

$$\theta_1 \text{ and } \theta_2 \text{ where } \theta_1 > \theta_2.$$

Heat is conducted in the direction of the fall of temperature. Quantity of heat conducted across the two opposite faces.

$$Q \propto A$$

$$Q \propto (\theta_1 - \theta_2)$$

$$Q \propto t$$

$$\propto \frac{1}{x}$$

$$Q \propto \frac{A(\theta_1 - \theta_2)}{x}$$

$$Q = \frac{KA(\theta_1 - \theta_2)t}{x}$$

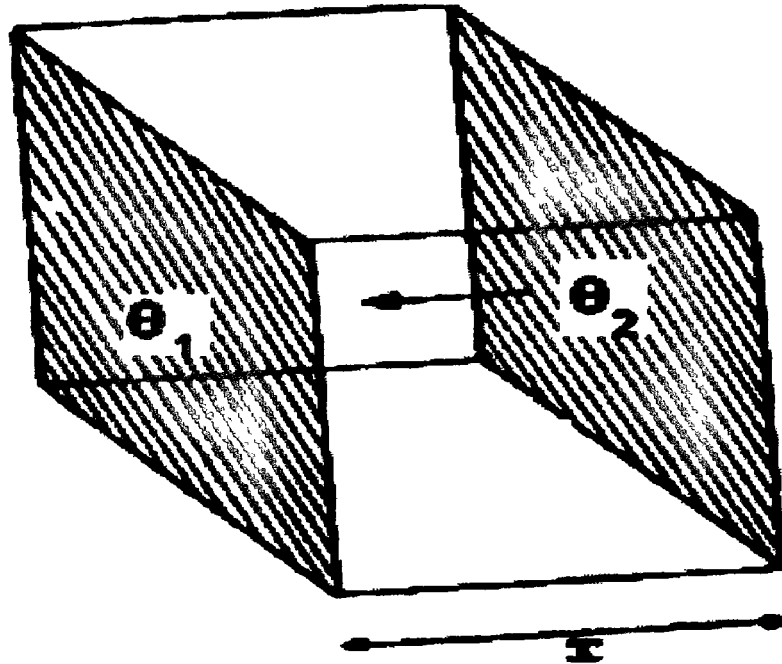


Fig 3.1

Here K is a constant called the coefficient of thermal conductivity of the material of the cube.

If $A = 1 \text{ sq cm}$, $(\theta_1 - \theta_2) = 1^\circ \text{C}$, $t = 1 \text{ s}$, $x = 1 \text{ cm}$; Then $Q = K$

Therefore, the coefficient of thermal conductivity is defined as the amount of heat flowing in one second across the opposite faces of a cube of side one cm maintained at a difference of temperature of 1°C .

Temperature gradient:

The quantity $\frac{\theta_1 - \theta_2}{x}$ represents the rate of fall of temperature with respect to distance. The quantity $\frac{dQ}{dx}$ represents the rate of change of temperature with respect to the distance. As temperature decreases with increases in distance from the hot end, the quantity $\frac{dQ}{dx}$ is negative and is called the temperature gradient.

$$Q = -KA \left[\frac{d\theta}{dx} \right] t$$

Dimension of K

$$K = - \frac{Q}{A \frac{d\theta}{dx} t} = - \frac{Q dx}{A d\theta t}$$

Q represents energy and its dimension, are,

$$[Q] = [ML^2T^{-2}],$$

$$[dx] = [L], [A] = [L^2], [d\theta] = [\theta], [t] = [T]$$

$$[K] = \frac{[ML^2T^{-2}], [L]}{[L^2][\theta][T]} = [ML^2T^{-3}\theta^{-1}]$$

Thermal Diffusivity:

It is defined as the ratio of thermal conductivity to thermal capacity per unit volume. Let the density of the substance be ρ and its specific heat S.

$$h = \frac{K}{\left[\frac{mS}{V}\right]} = \frac{K}{\rho S}$$

h is also called thermometric conductivity.

3.4 Rectilinear Flow of Heat along a Bar

Consider a bar of uniform area of cross – section which is heated at one end. Heat is flowing along the length of the bar. Consider two

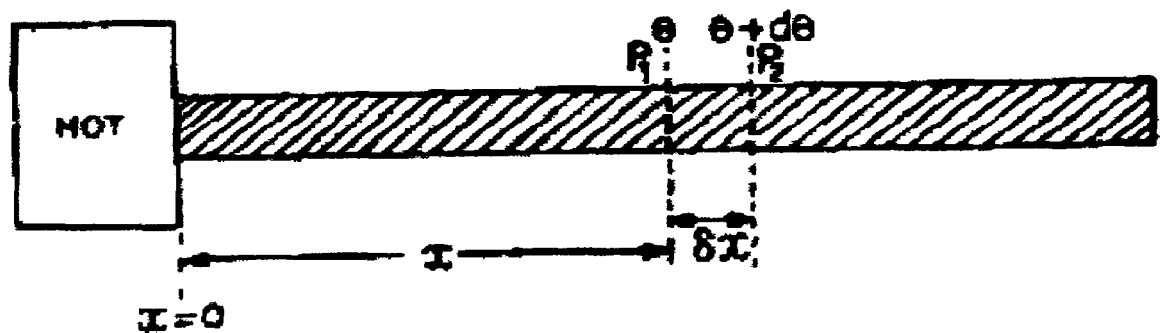


Fig 3.2

Planes P_1 and P_2 perpendicular to the length to the bar at distances x and $x+\delta x$ from the hot end. The temperature gradient at the plane $P_1 = \frac{d\theta}{dx}$, Here θ is the excess of temperature (above the surroundings) of the bar at P_1 . The excess of temperature at $P_2 = \theta + \frac{d\theta}{dx} \delta x$

The temperature gradient at $P_2 = \frac{d}{dx} \left(\theta + \frac{d\theta}{dx} \delta x \right)$

Heat flowing through P_1 in one second

$$Q_1 = -KA \frac{d\theta}{dx} \quad \text{----- (i)}$$

Heat flowing through P_2 in one second

$$Q_2 = -KA \frac{d}{dx} \left(\theta + \frac{d\theta}{dx} \delta x \right) \quad \text{----- (ii)}$$

Heat gained per second by the rod between the planes P_1 and P_2

$$\begin{aligned} Q_1 &= Q_1 - Q_2 \\ &= -KA \frac{d\theta}{dx} + KA \frac{d}{dx} \left(\theta + \frac{d\theta}{dx} \delta x \right) \\ Q &= KA \frac{d^2\theta}{dx^2} \delta x \quad \text{----- (iii)} \end{aligned}$$

Before the steady state is reached: The quantity of heat Q is used in two ways before the steady state is reached. Partly the heat is used to raise the temperature of the rod and the rest is lost due to radiation. Let the rate of rise of temperature of the bar be $\frac{d\theta}{dt}$.

The heat used per second to raise the temperature of the rod

$$\begin{aligned} &= \text{mass} \times \text{specific heat} \times \frac{d\theta}{dt} \\ &= (A \delta x) \rho S \frac{d\theta}{dt} \quad \text{----- (iv)} \end{aligned}$$

Where A is the area of cross section of the rod, ρ is the density of the material and S is the specific heat.

The heat lost per second due to radiation.

$$= \epsilon p \delta x \theta \quad \text{----- (v)}$$

Where E is the emissive power of the surface, p is the perimeter and θ is the average excess of temperature of the bar between the planes P_1 and P_2 .

$$Q = A \delta x \rho S \frac{d\theta}{dt} + \epsilon p \delta x \theta$$

Substituting the value of Q from equation (iii)

$$KA \frac{d^2\theta}{dx^2} \delta x = A \delta x \rho S \frac{d\theta}{dt} + \epsilon p \delta x \theta$$

$$\frac{d^2\theta}{dx^2} = \frac{\rho^2}{K} \frac{d\theta}{dt} + \frac{Ep}{KA} \theta \quad \text{----- (vi)}$$

This is the general equation that represents the rectilinear flow of heat along a bar of uniform area of cross –section.

Special Cases :

- (1) **When heat lost by radiation is negligible.** When the rod is completely covered by insulating materials, the heat lost by radiation $Ep. \delta x. \theta$ is zero. In that case the total heat gained by the rod is used to raise the temperature of the rod. From equation (vi)

$$\frac{d^2\theta}{dx^2} = \frac{\rho^S}{K} \frac{d\theta}{dt} = \frac{1}{h} \frac{d\theta}{dt} \quad \text{----- (vii)}$$

Here, $\frac{K}{\rho^S} = h$, the thermal diffusivity of the rod.

- (2) **After the steady state is reached:** When the steady state is reached, the rod does not require any further heat to raise its temperature. At this state.

$$\frac{d\theta}{dt} = 0$$

From equation (vi)

$$\frac{d^2\theta}{dx^2} = \frac{Ep}{KA} \theta$$

Taking

$$\frac{Ep}{KA} = \mu^2$$

$$\frac{d^2\theta}{dx^2} = \mu^2 \theta \quad \text{----- (viii)}$$

The general solution of this equation is

$$\theta = Ae^{+\mu x} + Be^{-\mu x} \quad \text{----- (ix)}$$

Where A and B are two unknown constants to be determined from the boundary conditions of the problem.

If the bar is sufficiently long, we can assume that under steady state, no heat is lost from the free end of the bar. This is due to the fact that nearly the whole of the heat energy is lost from the sides as radiation and the free end will be at the temperature of the surroundings.

(a) Suppose the bar is of infinite length.

Let the excess of temperature above the surroundings of the hot end be θ_0 and of the other end be zero.

$$\text{At } x=0, \theta = \theta_0$$

From equation (ix)

$$\theta_0 = A + B$$

$$\text{At } X=\infty, \theta = 0$$

From equation (ix),

$$0 = Ae^{\infty}$$

But e^{∞} cannot be zero, therefore, $A = 0$

$$\text{Taking } A = 0, \theta_0 = B$$

Substituting the value of A and B in equation (ix)

$$\theta = \theta_0 e^{-\mu x} \quad \text{-----(x)}$$

This equation represents the excess of temperature of a point at a distance x from the hot end after the steady state is reached and this represents an exponential curve. This equation is useful in Ingen-Hausz experiment.

(b) Suppose the bar is sufficiently long and is of finite length L. Then the boundary conditions are.

$$\text{At } x=0,$$

$$\theta = \theta_0$$

$$\frac{d\theta}{dx} = 0, \text{ at } x = L$$

The values of A and B in this case are.

$$A = \frac{\theta_0}{1 + e^{2\mu L}}$$

$$\text{and } B = \frac{\theta_0}{1 + e^{-2\mu L}}$$

The solution of equation (ix) will be

$$\theta = \theta_0 \left[\frac{e^{\mu s}}{1 + e^{2\mu L}} + \frac{e^{-\mu s}}{1 + e^{-2\mu L}} \right]$$

Ingen – Hausz Experiment

Ingen – Hausz devised an experiment to compare the thermal conductivities of several materials.

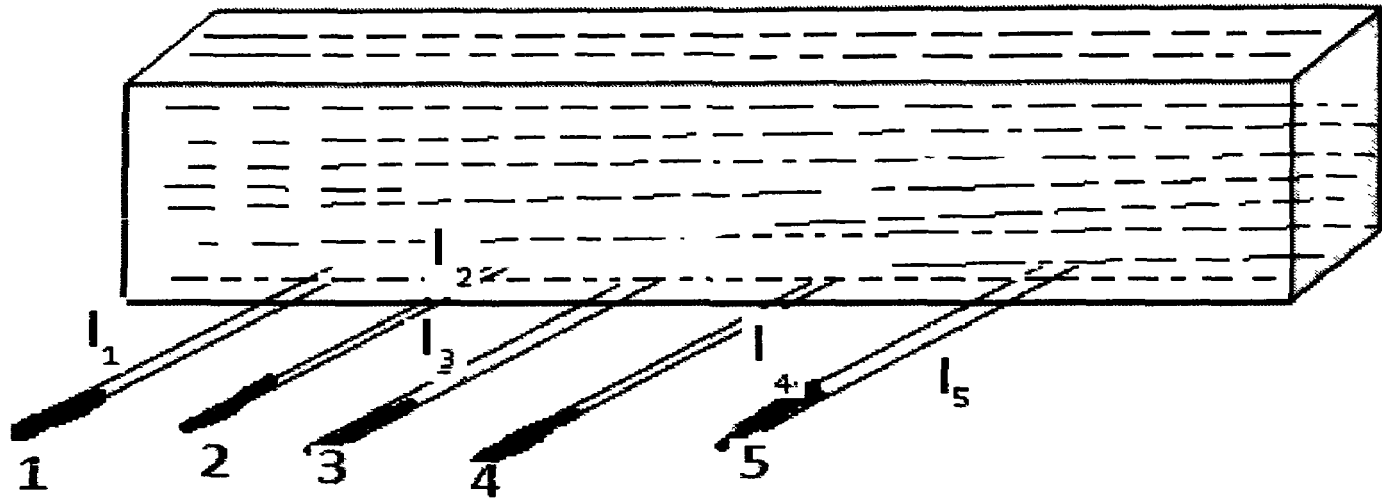


Fig 3.3

Take a box containing hot water or oil. Rods of different materials of the same length and area of cross-section (same size and shape) are taken. Their outer surfaces are electroplated with the same material and are equally polished. This is done such that the emissive power e for all the rods is the same. Rods are fixed at the base of the vessel (Fig.3.3) and their portions outside the vessel are coated uniformly with wax. It is found that the wax melts up to different lengths on different rods.

Let the length up to which the wax has melted be l_1, l_2, l_3, \dots etc., θ_0 be the excess of temperature of the hot bath above the room temperature and θ_m the excess of temperature of the melting point of wax above the room temperatures.

As,
$$\theta = \theta_0 e^{-\mu x}$$

For the first rod,

$$\theta_m = \theta_0 e^{-\mu_1 l_1}$$

For the second rod,

$$\theta_m = \theta_0 e^{-\mu_2 l_2}$$

For the Third rod,

$$\theta_m = \theta_0 e^{-\mu_3 l_3}$$

$$\begin{aligned} \therefore \theta_m &= \theta_0 e^{-\mu_1 l_1} = \theta_0 e^{-\mu_2 l_2} \\ &= \theta_0 e^{-\mu_3 l_3} \\ \therefore \mu_1 l_1 &= \mu_2 l_2 = \mu_3 l_3 = \dots \end{aligned}$$

But
$$\mu_1 = \sqrt{\frac{Ep}{K_1 A}}$$

$$\mu_2 = \sqrt{\frac{Ep}{K_2 A}}$$

$$\mu_3 = \sqrt{\frac{Ep}{K_3 A}}$$

Here, E, p and A are the same for all the rods.

$$\begin{aligned} \therefore l_1 \sqrt{\frac{Ep}{K_1 A}} &= l_2 \sqrt{\frac{Ep}{K_2 A}} \\ &= l_3 \sqrt{\frac{Ep}{K_3 A}} = \dots \end{aligned}$$

$$\begin{aligned} \therefore \frac{l_1}{\sqrt{K_1}} &= \frac{l_2}{\sqrt{K_2}} \\ &= \frac{l_3}{\sqrt{K_3}} = \text{Constant} \end{aligned}$$

$$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \text{Constant}$$

Thus, the normal conductivity of the material of the rod is directly proportional to the square of the length up to which the wax melts on the rod.

From equation (i), the thermal conductivities of any two materials can be compared. If the conductivity of one of the rods is known, the thermal conductivities of other rods can be determined. This experiment is not used for finding the thermal conductivity because the results obtained are not accurate. It is, however, useful for demonstration purposes.

3.5 Lee and Charlton's method for Bad Conductors

The apparatus consists of a cylindrical steam chamber A, the specimen disc D and brass or copper block C. The whole apparatus is suspended from the stand (Fig.3.4). T_1 and T_2 are the thermometers used to determine the temperature after the steady state is reached.

Steam is passed through the chamber and the readings of the thermometers T_1 and T_2 are noted after the steady state is reached. The heat passing through D in one second is equal to the heat radiated by the exposed surface of C in one second.

$$\frac{KA(\theta_1 - \theta_2)}{d} = mS \frac{d\theta}{dt} \left[\frac{A+S}{2A+S} \right] \quad \text{-----(i)}$$

Here $\left[\frac{A+S}{2A+S} \right]$ is the fraction of the total area exposed to the surroundings.

Here A is the area of cross-section of D and C. S is the area of the curved surface of C, $\frac{d\theta}{dt}$ is the rate of cooling at temperature θ_2 , m is the mass and s is the specific heat of C.

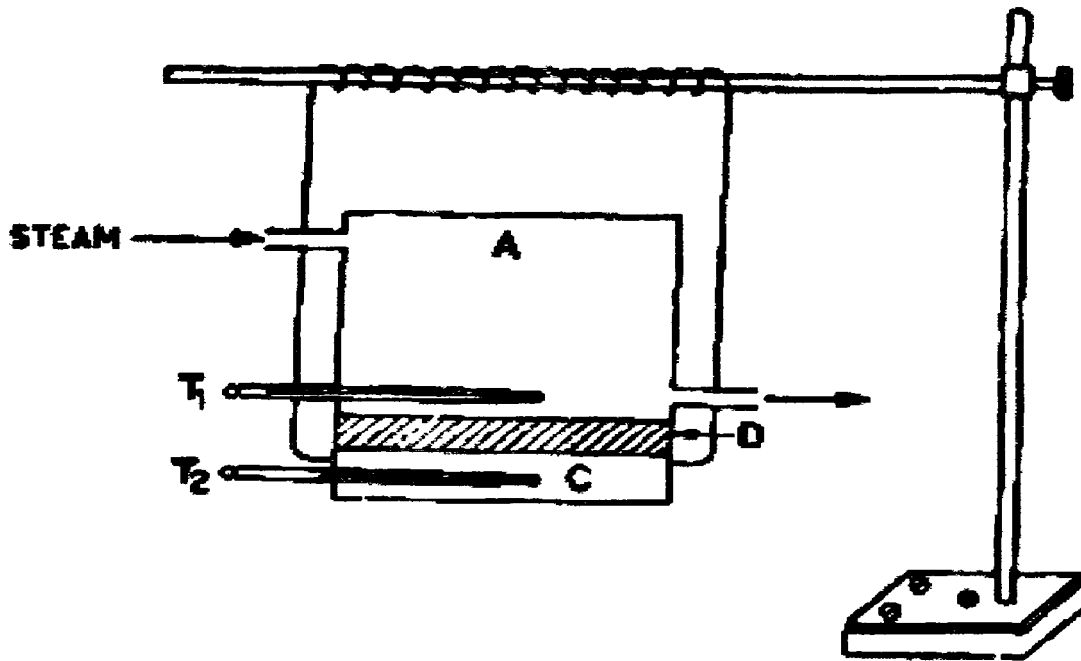


Fig 3.4

To find $\frac{d\theta}{dt}$, the disc D is removed and C makes contact with the steam chamber. C is removed when its temperature is about 10^0 C higher than θ_2 . It is placed over two knife edges and its temperature is observed after equal intervals of time (say one minute). A graph is drawn between temperature and time. From the graph, the value of $\frac{d\theta}{dt}$ at temperature θ_2 is found. From equation (i) K can be calculated

Check your progress

1. How is the effect of convection is eliminated in Lee's Method of finding K in air.

Ans: -----

Radiation: - Radiation is the process in which heat is transferred from one place to another directly without the aid of intervening medium. Heat from the sun reaches earth due to radiation without affecting the intervening medium.

3.6 Black Body:

A perfectly black body is one which absorbs all the heat radiations (corresponding to all wavelengths) incident on it. When such a body is placed inside an isothermal enclosure, it will emit the full radiation of the enclosure after it is in equilibrium with the enclosure. These radiations are independent of the nature of the substance. Such heat radiations in a uniform temperature enclosure are known as **black body radiation**. Also the black body completely absorbs heat radiations of all wavelengths. Thus the black body also emits completely the radiations of all wavelengths at that temperature. In practice, a perfectly black body is not available. A body showing close approximation to a perfectly black body can be constructed.

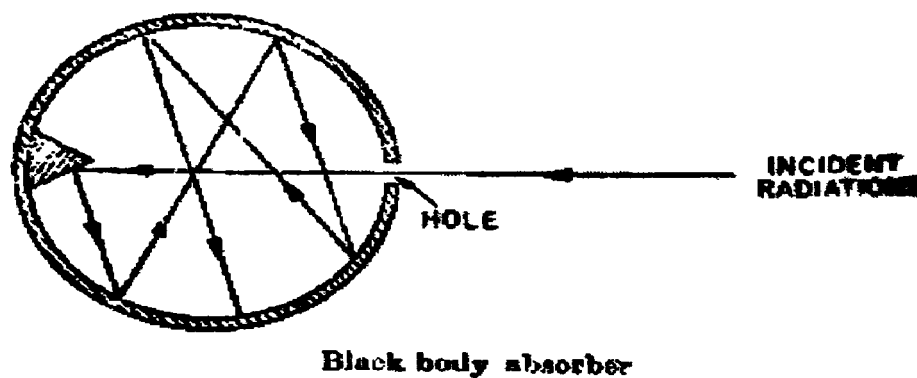


Fig 3.5

A hollow copper sphere is taken and is coated with lamp black on its inner surface [Fig. 3.5]. A fine hole is made and a pointed projection is made just in front of the hole.

When the radiations enter the hole, they suffer multiple reflections and are completely absorbed. This body acts as a black body absorber. When this body is placed in bath at a fixed temperature, the heat radiations come out of the hole [Fig. 3.6]. The hole acts as a black body radiator. It should be remembered that only the hole and not the walls of the body, acts as the black body radiator.

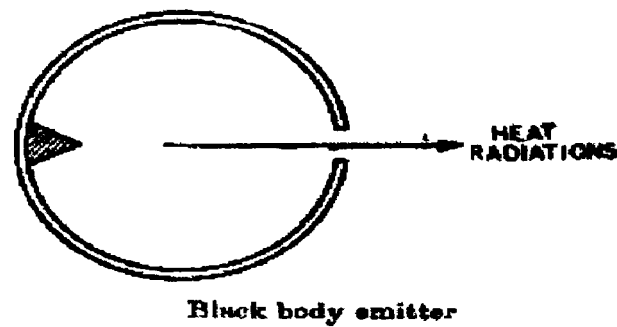


Fig 3.6

Wien also constructed a black body in the form of a cylinder. This black body is commonly used now a days.

It consists of a hollow metallic cylinder and fitted with heating coils wound around it. The inner surface of the cylinder is coated with lamp black. The cylinder is placed in concentric porcelain tubes (Fig.3.7); the temperature is measured with the help of a thermocouple arrangement. Heat radiations emerge out of the hole.

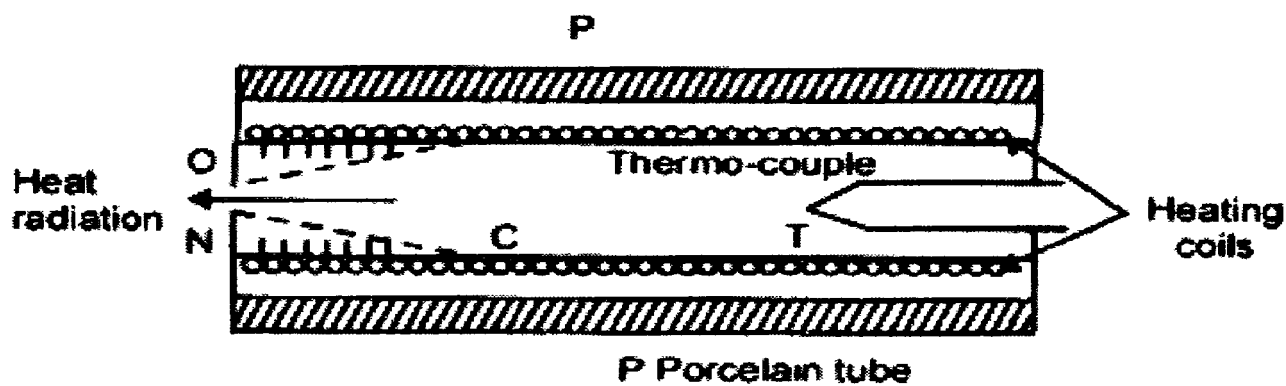


Fig 3.7

The radiations from the inner chamber can be limited with the help of diaphragms provided on the inner side. This hole will act as a black body radiator.

Wien's Displacement Law . From thermodynamical considerations, Wien has shown that the product of the wavelength corresponding to maximum energy and absolute temperature is constant

$$\lambda_m \times T = \text{constant} = 0.2892 \text{ cm}^{-K} \quad \text{----(i)}$$

This is called Wien's displacement law. It also shows that with increase in temperature, λ_m decreases. Wien has also shown that the energy E_{max} is directly proportional to the fifth power of the absolute temperature.

$$E_m \propto T^5$$

$$E_m = \text{constant} \times T^5 \quad \text{----(ii)}$$

Wien deduced the radiation law for the energy emitted at a given wavelength λ and at a temperature T.

$$E_{\lambda} = \lambda^{-5} f(\lambda T) \quad \text{-----(iii)}$$

With certain assumptions Wien was able to deduce the relation

$$E_{\lambda} = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \quad \text{----- (iv)}$$

Here C_1 and C_2 are constants

Equation (iv) represents the Wien's law of distribution of energy.

Check your progress

2. What is the most important use of Wien's Law?
3. What are the demerits of Wien's displacement Law?

Ans: -----

Rayleigh-Jean's Law: The energy distribution in the thermal spectrum according to Rayleigh, is given by the formula.

$$E_{\lambda} = \frac{8\pi kT}{\lambda^4} \quad \text{-----(v)}$$

Here k is the Boltzmann's constant

The experimental results of Lummer and Pringsheim in the infra red region, however, show that the Wien's law holds good only in the region of shorter wavelengths. It does not hold good at longer wavelengths. The Rayleigh-Jean's law holds good in the region of longer wavelengths but not for shorter wavelengths. This was shown by Rubens and Kurlbaum. Thus Wien's law and Rayleigh-Jean's law do not precisely agree with the experimental results.

Planck's Law. Planck (1901) was able to derive a theoretical expression for the energy distribution on the basis of quantum theory of heat radiations. According to quantum theory, energy is emitted in the form of packets or quanta called photons. Each photon has an energy $h\nu$ where h is the Planck's constant and ν is the frequency of radiation. According to this theory, the body does not emit energy continuously but not only in certain multiples of the fundamental frequency of the

resonator (energy emitter). As the energy of a photon is $h\nu$, the energy emitted is equal to $h\nu, 2h\nu, 3h\nu, \dots$ etc. He deduced the formula.

$$E_\lambda = \frac{8\pi hc}{\lambda^5 [e^{\frac{h\nu}{kT}} - 1]} \quad \text{----- (vi)}$$

Here c is the velocity of electromagnetic waves ($=3 \times 10^8$ metres per second)

Equation (vi) agrees with the experimental results.

(i) For shorter wavelengths

$$e^{\frac{h\nu}{kT}} > 1$$

From equation (vi),

$$A \quad E_\lambda = 8\pi hc \lambda^{-5} e^{-\frac{h\nu}{kT}}$$

$$E_\lambda = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} \quad \text{----- (vii)}$$

Where

$$C_1 = 8\pi hc \text{ and } C_2 = \frac{hc}{\lambda}$$

Equation (vii) represent's Wien's radiation law.

(ii) For longer wavelengths, $\frac{h\nu}{kT}$ is small.

From equation (vi), expanding $e^{\frac{h\nu}{kT}}$ and neglecting higher power,

$$E_\lambda = \frac{8\pi hc}{\lambda^5 [1 + \frac{h\nu}{kT} - 1]}$$

$$= \frac{8\pi hc, \lambda kT}{\lambda^5 \cdot hc}$$

$$E_\lambda = \frac{8\pi kT}{\lambda^4} \quad \dots \text{ (viii)}$$

Equation (viii) represents Rayleigh-Jean's law.

Thus Planck's formula for the energy distribution in a thermal spectrum is applicable for all wavelengths.

Check your progress

4. What are the special features of the Planck's theory?

Ans: -----

3.7 Stefan's Law

The experimental study of the rate of emission of heat energy by a hot body by Tyndall helped Stefan (in 1879) to enunciate the law called Stefan's law. In 1884, Boltzmann gave a theoretical proof of Stefan's law on the basis of thermodynamics. Therefore, this law is also called Stefan-Boltzmann law.

According to this law, the rate of emission of radiant energy by unit area of a perfectly black body is directly proportional to fourth power of its temperature.

$$R \propto T^4 \text{ or } R = \sigma T^4 \text{ ---- (i)}$$

Where σ is called Stefan's constant. If the body is not perfectly black and its emissivity or relative emittance is e , then

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

Hence e varies between zero and one, depending on the nature of the surface. For a perfectly black body $e = 1$. The law is not only true for emission but also for absorption of radiant energy. The hot body will continue emitting heat up to zero degree absolute temperature, if the temperature of the surroundings is zero degree absolute. But, in actual practice, the hot body is surrounded by a wall at some lower temperature. Due to this the body is continuously emitting and absorbing the heat radiations. When the body has the same temperature as that of the surroundings, the rate of emission and absorption are equal.

Hence, if a perfectly black body at temperature T_1 is surrounded by a wall (surroundings) at a temperature T_2 the net rate of loss (or gain) of heat energy per unit area of the surface is given by,

$$R \propto (T_1^4 - T_2^4)$$

$$R = \sigma(T_1^4 - T_2^4) \text{ --(iii)}$$

If the body has an emissivity e ,

Then

$$R = e\sigma(T_1^4 - T_2^4) \quad \text{----- (iv)}$$

Experimental Verification of Stefan's Law

In 1987, Lummer and Pringsheim experimentally verified Stefan's law over a wide range of temperature (100°C to $1,300^\circ\text{C}$).

The apparatus consisted of a black body. For temperatures between 200°C and 600°C , a hollow copper sphere coated inside with platinum black was used. The fused nitrates of sodium and potassium having a melting point of 219°C were used as the bath surrounding the black body. For temperature between 900°C and 1300°C , an iron cylinder coated inside with platinum black was used as a black body and it was enclosed in a double walled gas furnace. A thermocouple T was used as a thermometer. A bolometer B was used to measure the intensity of the emitted heat radiations. S_1 , S_2 and S_3 were the water-cooling shutters (Fig.3.8).

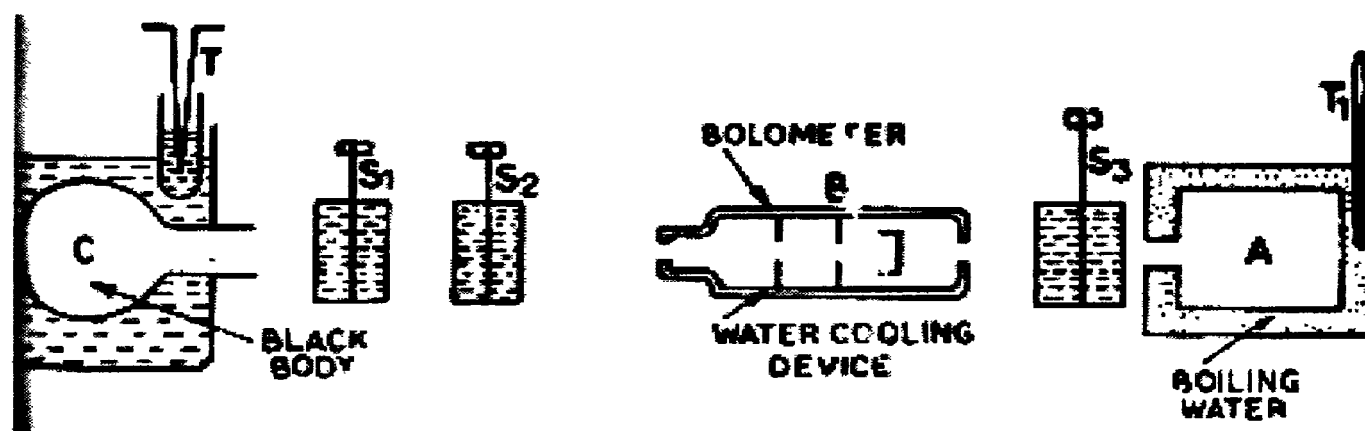


Fig 3.8

Another black body A at 100°C was used to standardize the bolometer. The double walled vessel of the black body A contained boiling water at 100°C . The bolometer B was allowed to face the opening of the black body A and the shutter S_3 raised. The deflections in the galvanometer of the bolometer at various distances were noted and it was found that the deflection was inversely proportional to the square of the distance between the bolometer and the opening of the black body A . Thus the deflection in the galvanometer was proportional to the intensity of heat radiations.

Thus shutter S_3 was closed and the bolometer B was allowed to face the opening of the black body C . The shutters of S_1 and S_2 were raised. The bath surrounding the black body was maintained at a constant temperature and the

maximum deflection produced in the galvanometer of the bolometer was noted. Thus at various constant temperatures of the black body, corresponding to constant deflections (in the galvanometer of the bolometer) were observed. Then the data was reduced to a common arbitrary unit in terms of the total radiations from the black body A at 100°C.

Let θ be the deflection in the galvanometer, T_1 the temperature of the black body and T_2 , the temperature at the entrance of the bolometer. It was found that

$$\theta \propto (T_1^4 - T_2^4)$$

But

$$\theta \propto R$$

$$\theta \propto (T_1^4 - T_2^4)$$

This verifies Stefan's law.

Recently Coblentz has verified Stefan's law more accurately. He took an electrically heated black body whose temperature was measured by an accurate thermocouple. An absolute bolometer was used to measure the amount of heat radiations emitted by the black body. He was able to show the correctness of Stefan's law experimentally up to 1,600°C.

Solar Constant

The sun is the source of heat radiation and it emits heat radiations in all directions. The earth receives only a fraction of the energy emitted by the sun. the atmosphere also absorbs a part of the heat radiations and air, clouds, dust particles etc. in the atmosphere scatter the heat and light radiations falling on them. From the quantity of heat radiations received by the earth, it is possible to estimate the temperature of the sun. Therefore, to determine to value of a constant, called *solar constant*, certain ideal conditions are taken into consideration.

Solar Constant. *It is the amount of heat energy (radiation) absorbed per minute by one sq cm of a perfectly black body surface placed at a mean distant of the earth from the sun, in the absence of the atmosphere, the surface being held perpendicular to the sun's rays.*

The instruments used to measure the solar constant are called **pyrheliometers**. The heat energy absorbed by a known area in a fixed time is found with the help of the pyrheliometers. To eliminate the effects of absorption

by the atmosphere, the value of the solar constant is found at various altitudes of the sun on the same day under similar sky conditions. If S is the observed solar constants, S_0 the true solar constant and Z the altitude (angular elevation) of the sun, then

$$S = S_0 a^{\sec Z} \quad \text{---- (i)}$$

$$\text{or } \log S = \log S_0 + \sec Z \log a \quad \text{---(ii)}$$

Here a is a constant.

A graph is plotted between $\log S$ along the y-axis and $\sec Z$ along the x-axis. The graph is a straight line. Produce the graph to meet the y-axis. The intercept on the y-axis gives $\log S_0$. From the value of $\log S_0$, the value of S_0 , the solar constant can be calculated. The value obtained varies between 1.90 and 2.60 calories per sq cm per minute.

Water Flow Pyrheliometer

This instrument was designed by Abbot and Fowle. It consists of a cylindrical double walled vessel A. The lower side is conical in shape and is coated with platinum black on its inner side. T_1 and T_2 are the platinum resistance thermometers to record the temperatures of incoming and outgoing water (Fig.8.50)

D is a diaphragm which allows the heat radiations from the sun through a known area of cross-section. Heat radiations are allowed to enter the vessel A and the rate of flow of water is adjusted so that the thermometers T_1 and T_2 show constant temperatures (say θ_1 and θ_2). The spiral coil helps water in making good contact with the walls. After the steady has been reached i.e., T_1 and T_2 show constant temperatures, the heat radiations from the sun are cut off

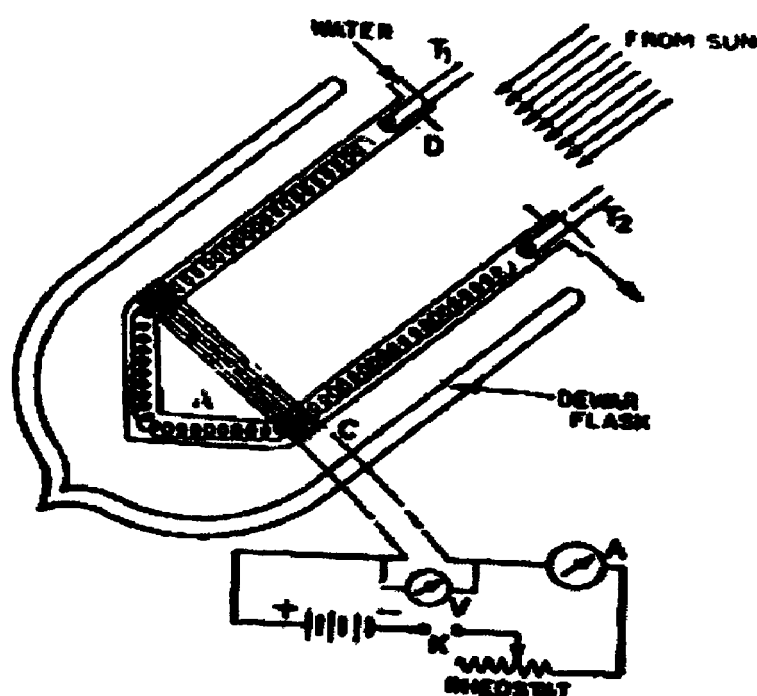


Fig 8.50

Now a suitable current is passed through the manganin coil c so that the same conditions are restored i.e., the thermometers T_1 and T_2 show the same constant temperatures θ_1 and θ_2 . If E volts is the potential difference and I amperes is the current flowing through the manganin coil, then the amount of heat produced per second = $\frac{EI}{4.2}$ cal. Therefore, the amount of heat radiations received from the sun in one minute by the exposed surface of the vessel $A = \frac{EI \cdot 60}{4.2}$ cal. From this value, the solar constant can be calculated.

3.8 Let us sum-up

- The coefficient of thermal conductivity is defined as the amount of heat flowing in one second across the opposite faces of a cube of side one cm maintained at a difference of temperature of 1°C .
- It is defined as the ratio of thermal conductivity to thermal capacity per unit volume.
- Ingen-Hausz experiment is used to compare the thermal conductivities of several materials. 'K' is directly proportional to the square of the length up to which the wax melts on the rod.
- A perfectly black body is one which absorbs all the heat radiations (corresponding to all wavelengths) incident on it.
- **Wien's displacement law** - *the product of the wavelength corresponding to maximum energy and absolute temperature is constant.*
- **Stefan's law** - *the rate of emission of radiant energy by emit area of a perfectly black body is directly proportional to fourth power of its temperature.*

- **Solar Constant.** *It is the amount of heat energy (radiation) absorbed per minute by one sq cm of a perfectly black body surface placed at a mean distant of the earth from the sun, in the absence of the atmosphere, the surface being held perpendicular to the sun's rays.*

3.9 Unit – End Exercises

1. Define coefficient of thermal conductivity. What are its dimensions?
2. Discuss the rectilinear flow of heat along a bar of uniform area of cross-section. Describe expression for thermal conductivity and temperature distribution for a cylindrical rod heated along its axis.
3. Discuss Ingen-Hausz experiment to compare the thermal conductivity of different materials.
4. Discuss Lee's disc method for finding the co-efficient of thermal conductivity for bad conductors. Can this method be used for good conductors?
5. Deduce Wien's displacement law for the distribution of energy in black body spectrum?
6. State and explain Rayleigh-Jeans law.
7. Discuss Planck's hypothesis of quantum theory of radiation
8. State Stefan's law and write its equation. Explain how would you calculate surface temperature of the sun using the law.
9. What do you understand by a black body? State and explain Stefan's Law of heat radiation. Describe an experiment to verify Stefan's Law.
10. Define solar constant. Describe water flow pyrhelimeter and explain how solar constant is determined from it.

3.10 Problems for discussion

1. How much heat is lost through the outside wall of a dormitory room in 8 hours when the average outside temperature is 15°C and the average inside temperature is 22°C ? The wall is 2.5m, by 3.0m, is 0.15, thick and has an average thermal conductivity of 0.850w/m/k .
2. In Lee's disc experiment two discs are separated by a gap of 5mm thickness. The gap contains a gas of thermal conductivity $3.88 \times 10^{-5} \text{ w/m/k}^{-1}$. At steady state the temperatures of the two discs are 368K and 333K. If the area of cross section of the slab is 25 cm^2 calculate the quantity of heat crossing the gas per second.
3. Calculate the radiant emittance of a black body at a temperature of (i) 400K (ii) 4000K. [σ is $5.672 \times 10^{-8} \text{ M.K.S units}$]

4. Calculate the surface temperature of the sun and moon, given that $\lambda_m = 4753 \text{ \AA}$ and 14μ respectively, λ_m being wavelength of maximum intensity of emission.
5. What is the wavelength at which human body radiates maximum energy?

3.11 Answers to check your progress and problem for discussion

Check your progress

1. **Ans:** Convection is eliminated by allowing the heat to flow in the downward direction.
2. **Ans :** Evaluation of the surface temperature of the Sun.
3. **Ans :**
 - (i) It is based on classical mechanics, which is totally irrelevant in radiation problems.
 - (ii) Wien's value agreed only in shorter wavelength region.
4. **Ans:** Energy is radiated not continuously but in small indivisible packet called quanta

Energy of each quanta $E = h\gamma$ where h is the Planck's constant and γ is the frequency of radiation.

Answers to problem for discussion:

Solution 1:

$$\begin{aligned} \text{Heat conducted } Q &= \frac{\kappa A[\theta_2 - \theta_1]t}{d} = 0.850 \times 7.5 \times 37 \times 9 \times 3600 / 0.150 \\ &= 4.53 \times 10^7 \text{ J} \end{aligned}$$

Solution 2:

$$\begin{aligned} Q &= \frac{\kappa A[\theta_2 - \theta_1]t}{d} = 3.88 \times 10^{-5} \times 25 \times 10^{-4} \times 35 / 5 \times 10^{-3} \\ &= 679 \times 10^{-6} \text{ J/ Sec} \end{aligned}$$

Solution 3: $E = e\sigma T^4$ (e = 1, for a black body)

$$= \sigma T^4$$

$$\begin{aligned} \text{(i) } T &= 400\text{K} \\ E &= 5.672 \times 10^{-8} \times [400]^4 \\ &= 1452 \text{ watts/ m}^2 \end{aligned}$$

(ii) $T = 4000 \text{ K}$
 $E = 14520 \text{ k watts/ m}^2$

Solution 4:

$$\lambda_m T = \text{constant} = 0.2898$$

(i) for Sun $T_s = 0.2898 / 4753 \times 10^{-8} = 6097 \text{ K}$

(ii) for moon $T_m = 0.2898 / 14 \times 10^{-8} = 207 \text{ K}$

Solution 5:

$$\lambda_m T = \text{constant} = 0.2898$$

Temperature of the Human body $T = 37^\circ\text{C} = 273 + 37 = 310 \text{ K}$

Considering Human body as a black body,

$$\lambda_m = 2.898 \times 10^{-3} / 310 = 9.35 \times 10^{-6} \text{ m}$$

3.12 Suggested Readings:

1. Thermal physics- R.Murugesan , S.Chand S.Chand & Co, New Delhi..
2. Heat and Thermodynamics -J.B.Rajram and C.L.Arora, S.Chand & Co, New Delhi,2004.
3. Heat, Thermodynamics and Statistical Physics Brijlal, Dr. N. Subramanyam and P. S. Hemne.Revised edition, Reprint 2012 S.Chand& Company Ltd., New Delhi
4. Thermodynamics and Statistical Physics Singhal, Agarwal, SathyaPrakash 12thedition, 2008,PragatiPrakashan, Meerut
5. Thermodynamics, Statistical thermodynamics and Kinetics Thomas Engal, Philip Reid 1st edition, 2007, Dorling Kindersley (India) Pvt Ltd, New Delhi.

UNIT 4

Structure

4.1 Introduction

4.2 Objectives

4.3 Zeroth and First law of thermodynamics

4.4 Reversible and Irreversible process, Second law of thermodynamics

4.5 Heat engine - Derivation for efficiency

4.6 Carnot theorem

4.7 Entropy – change in entropy in reversible and irreversible process

change in entropy in conversion of ice into steam

4.8 Third law of thermodynamics

4.9 Let us sum up

4.10 Unit –end exercises

4.11 Problems for discussion

4.12 Answers to Check your progress

4.13 Suggested readings.

4.1 Introduction

Thermodynamics is branch of Physics which mainly deals with the transformation of heat into mechanical work. Today, the scope of thermodynamics has very much increased covering all the branches of physics, chemistry and engineering and has innumerable applications. Thermodynamics does not take into account the atomic constitution of matter *i.e.*, structure etc. but it only deals with the large scale response (macroscopic properties) of the system that we can observe and measure in experiments.

The Zeroth law of thermodynamics introduces the concept of temperature and the concept of thermodynamic equilibrium when two objects attain the same temperature when brought in thermal contact. During the process of reaching thermal equilibrium, heat is transferred between the objects. The first law of

thermodynamics represents the relationship between heat and mechanical work while the second law depicts the manner in which these energy changes take place. In short, thermodynamics is an empirical and experimental science and based upon the general laws of nature which govern the conversion of heat in to mechanical work and vice-versa.

4.2 Objectives

After going through this unit, you will be able to:

- explain the concept of temperature using the Zeroth law of Thermodynamics
- understand the significance of the first law of thermodynamics
- distinguish between a reversible and irreversible process
- define entropy
- calculate the change in entropy for reversible and irreversible change
- State the consequence of the third law of Thermodynamics

4.3 Zeroth law of thermodynamics:

The sense of touch is the simplest way to distinguish hot bodies from cold bodies. By touch we can arrange bodies in the order of their hotness. We speak of this as our *temperature sense*. This is a very subjective procedure for determining the temperature of a body and certainly not very useful for purposes of science. Further, the range of our temperature sense is limited. What we need is an objective, numerical, measure of temperature.

The first step toward attaining an objective measure of the temperature sense is to set up a criterion of *equality* of temperature. Let an object A which feels cold to the hand and an identical object B which feels hot be placed in contact with each other. After a sufficient length of time, A and B give rise to the same temperature sensation. Then, A and B are said to be in *thermal equilibrium* with each other. Two bodies are in thermal equilibrium means that the two bodies are in states such that, if the two were connected, the combined system would be in thermal equilibrium. If two bodies are in thermal equilibrium when placed in contact, then by definition their *temperatures are equal*. Conversely, if the temperatures of two bodies are equal, they will be in thermal equilibrium when placed in contact.

The logical and operational test for thermal equilibrium is to use a third or test body such as a *thermometer*. This is summarised in a postulate often called the zeroth law of thermodynamics.

Statement: *If A and B are in thermal equilibrium with a third body C (the thermometer), then A and B are in thermal equilibrium with each other.*

Explanation: Thus if we want to know when two beakers of water are at the same temperature it is unnecessary to bring them into contact and see whether their properties change with time. We insert a thermometer (body C) in one beaker of water (body A) and wait until some property of the thermometer, such as the length of the mercury column in a glass capillary, becomes constant. Then by definition, the thermometer has the same temperature as the water in the beaker A. We next repeat the procedure with the other beaker of water (body B). If the lengths of the mercury columns are the same, the temperatures of A and B are equal. Experiment shows that if the two beakers are brought into contact, no changes in their properties take place.

Significance: This law forms the basis of concept of temperature. All these three systems can be said to possess a property that ensures their being in thermal equilibrium with one another. This property is known as temperature. We may, therefore, define the temperature of a system as the property that determines whether or not the system is in thermal equilibrium, with the neighbouring systems. It is obvious that if two systems are not in thermal equilibrium, they will be at different temperatures. Speaking loosely, the essence of the zeroth law is: there exists a useful quantity called temperature.

First Law of thermodynamics

Statement: The amount of heat supplied to a system is equal to the algebraic sum of the change in internal energy of the system and the amount of external work done by the system.

Explanation. The differential form of the first law of thermodynamics is

$$dQ = dU + dW$$

dQ = amount of heat supplied to the system

dU = increase in internal energy of the system

dW = external work done by the system

In all transformations, the energy due to heat units supplied must be balanced by the external work done plus the increase in internal energy.

In the first law, a conversion between heat and mechanical energies (work) is set up and in the balancing process, internal energy U is defined.

When a cold body is placed in contact with a hot body, first law says that the heat gained by the colder body is equal to heat lost by the hotter body when equilibrium is attained. The first law does not specifically say that heat does not flow spontaneously from the colder to the hotter body. The fact that heat can only pass from a hot body to a colder body and not otherwise is not covered by first law. First law is, therefore, insufficient for the sake of completeness of thermodynamic studies. To cover the directional properties of heat, it is desired to define some law. This is the basis of the second law of thermodynamics.

Significance of the first law: The first law of thermodynamics establishes the relation between heat and work. According to this law, heat can be produced only by the expenditure of energy in some form or the other. Hence it follows directly from this law that it is impossible to make a perpetual motion machine or to derive work without any expenditure of energy.

Application of the first law: From the first law of thermodynamics.

$$dQ = dU + P dV$$

the thermal energy of a system U is a function of any two of P , V and T . choosing T and V .

$$U = f(T, V)$$

We have, $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

Therefore, the first law becomes

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$$

Dividing by dT , we get

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}$$

This equation is true for any process involving any temperature change dT and any volume change dV .

(a) If V is constant, $dV = 0$ and

$$\left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_v$$

Hence C_v is the molar specific heat capacity at constant volume.

(b) If P is constant, Eq.(5) becomes

$$\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P$$

But, $\left(\frac{dQ}{dT}\right)_P = C_p =$ *Molar specific heat capacity at constant pressure.*

$$C_p = C_v + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P$$

For a perfect gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$. Further

$$PV = RT \text{ or } P \left(\frac{\partial V}{\partial T}\right)_P = R.$$

Eq.(7) becomes $C_p = C_v + R$

Check your progress

1. If 100 joules of heat is added to a system that does no external work, by how much is the internal energy is raised?

Ans:

.....

.....

4.4 Reversible process

Thermodynamically, a reversible is one which an infinitesimally small change in the external conditions will result in all changes taking place in the direct process being exactly repeated in the reverse order and opposite sense.

It means that in a step where heat is absorbed in the process, it is given out in the reverse process and vice versa. Similarly, in a step where work is done by the working substance in the direct process, an equal amount of work is done on the working substance in the reverse process

The process will not be reversible if there is any loss of heat due to friction, radiation or conduction. If the changes take place rapidly, the process will not be reversible.

The conditions of reversibility for any heat engine or process are:

1. The pressure and temperature of the working substance must not differ appreciably from those of the surroundings at any stage of the cycle of operation.
2. All the processes taking place in the cycle of operation must be infinitely slow.
3. The working parts of the engine must be completely free from friction. There should not be any loss of energy due to conduction or radiation during the cycle of operation.

Examples: 1. All isothermal and adiabatic changes are reversible when performed slowly. Under these conditions if heat is supplied to a given mass of a gas at constant pressure, it expands and does some external work. If the same amount of work is done on the gas in compressing it, the same quantity of heat will be given out.

2. Ice melts when a certain amount of heat is absorbed by it. The water so formed can be converted into ice if the same amount of heat is removed from it.

It should be remembered that the conditions mentioned for reversible processes can never be realised in practice. Hence, a reversible process is only an ideal concept. In actual process, there is always loss of heat due to friction, conduction, radiation, etc.

Check your progress
2. What are the most important conditions of reversibility?
Ans:
.....
.....

Irreversible process

Any process which is not reversible exactly is an irreversible process.

Irreversible processes can also be defined as those processes which can not be retraced in the opposite order by reversing the controlling factors.

All natural processes such as conduction, radiation, radioactive decay, etc., are irreversible processes.

Examples: 1. Production of heat by friction is an irreversible process because heat will again be produced (and not absorbed) if the direction of motion is reversed.

2. Heat produced by the passage of a current through a resistance is irreversible. It is because even when the current is reversed, the same effect is observed.

3. Practical examples of irreversible processes are conduction of heat from a hot body to colder one, diffusion of liquids and gases, Joule-Thomson expansion, etc.

Check your progress

3. State to which category the following processes belong; (Reversible / Irreversible)

- a) isothermal expansion
- b) adiabatic expansion
- c) conduction, convection and radiation
- d) friction
- e) heating by electric current

Ans: -----

Second Law of thermodynamics:

There are two conventional statements of second law of thermodynamics.

- (i) **Clausius statement.** It is impossible for self-acting machine, unaided by any external agency, to transfer heat from a body at a lower temperature to a body at a higher temperature, or heat cannot of itself pass from a cold to a hot body.

Explanation: This statement implies that to convey heat continuously from a cold to a hot body, it is necessary to supply work by an outside agent. We know from experience that when two bodies are in contact, heat energy flows from the hot body in such a case and so determines the direction of transfer of heat. The direction can be reversed only by an expenditure of work. This takes place in a refrigerator in which electrical energy is used to pump heat from the cool interior to the warmer room.

It is impossible to construct a refrigerator that works without the supply of energy.

- (ii) **Kelvin-Planck statement.** It is impossible to construct a device which, operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work.

Explanation:. According to this statement, a single reservoir at a single temperature cannot continuously transfer heat into work. This statement implies that we cannot produce mechanical work by extracting heat from a single reservoir without returning any heat to a reservoir at a lower temperature. As an example, it is impossible to drive a steamship across the ocean by extracting heat from the ocean.

Hence, heat can be converted into work only if a body at a higher temperature and another at a lower temperature are available.

4.5 Heat Engine:

Heat engine is a device which converts heat into work. A heat engine, in general, consists of three parts.

1. A source or high temperature reservoir at temperature T_1
2. A sink or low temperature reservoir at temperature T_2
3. A working substance.

In a cycle of heat engine, the working substance extracts heat Q_1 from source, does some work W and rejects remaining heat Q_2 to sink (Fig.4.1)

Efficiency of heat engine

$$\eta = \frac{\text{Work done } (W)}{\text{Heat taken from source } (Q_1)}$$
$$= \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} = \frac{T_1 - t_2}{T_1}$$

This is general expression for the efficiency of heat engine.

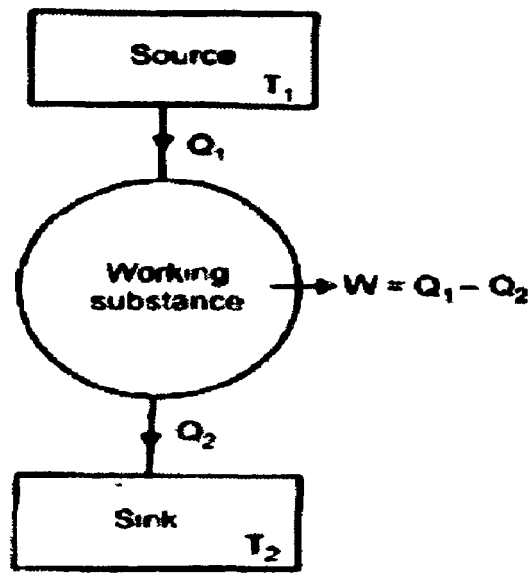


Fig 4.1

Carnot's engine consists of the following parts

- (1) Source.** A source is a hot body at a constant temperature T_1K . The heat engine can draw heat from the source (Fig 4.2)
- (2) Sink.** The sink is a cold body at a constant lower temperature T_2K . Any amount of heat can be rejected to the sink
- (3) Working substance.** The working substance is an ideal gas enclosed in a cylinder-piston arrangement.

A perfectly non-conducting stand is also provided so that the working substance can undergo adiabatic operation.

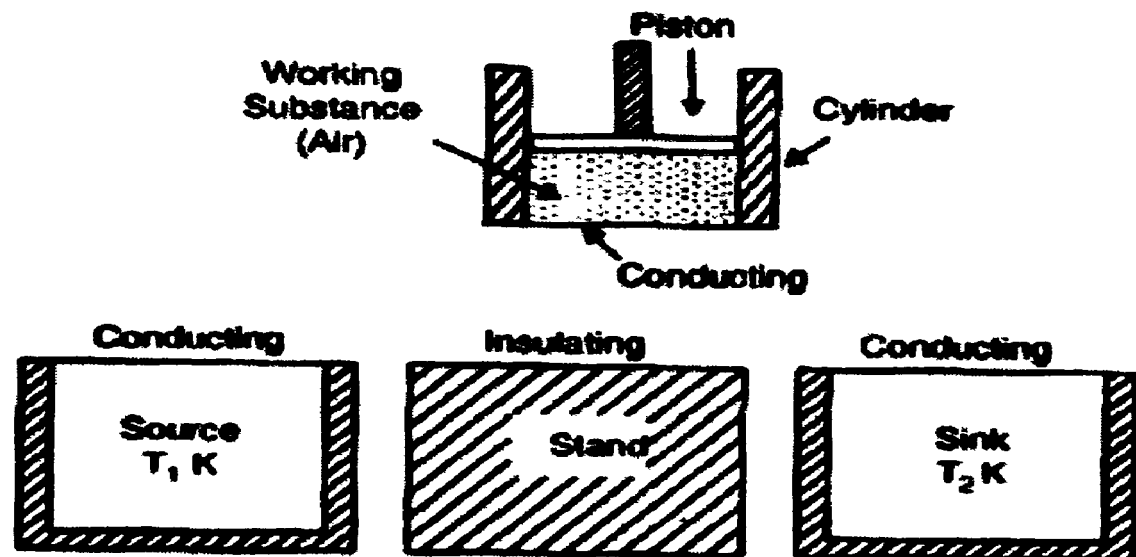


Fig 4.2

Carnot's cycle

(i) Isothermal expansion AB. Place the cylinder on the source at temperature T_1 .

the piston is moved slowly upward so that the gas expands isothermally. The isothermal expansion of the gas is represented by the curve AB (Fig.4.3)

Consider one gram molecule of the gas

Let the quantity of heat absorbed from the source be Q_1 .

This is equal to the amount of work done W_1 by the gas in the expansion from initial state (P_1, V_1) to final state (P_2, V_2) .

$$Q_1 = W_1 = \int_{V_1}^{V_2} P dV = RT_1 \int_{V_1}^{V_2} \frac{dV}{V} = RT_1 \log_e \left(\frac{V_2}{V_1} \right)$$

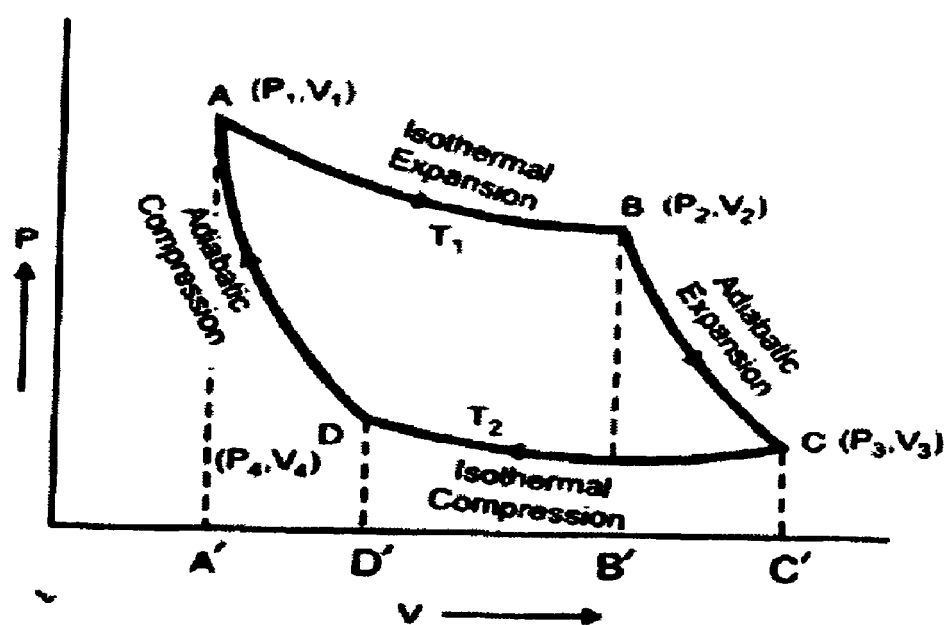


Fig 4.3

(ii) Adiabatic expansion BC. Place the cylinder on the insulating stand. Allow the gas to expand adiabatically till the temperature falls to T_2 . The change is represented by the adiabatic BC.

The work done by the gas W_2 is given by

$$W_2 = \int_{V_2}^{V_3} P dV = \int_{V_2}^{V_3} K \frac{dV}{V^\gamma} = \left[\frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma} \right]$$

$$= \left[\frac{P_3V_3 - P_2V_2}{1-\gamma} \right] \quad (\text{since } P_2V_2^\gamma = P_3V_3^\gamma = K)$$

$$= \left[\frac{RT_2 - RT_1}{1-\gamma} \right]$$

$$(P_2V_2 = RT_1 \text{ and } P_3V_3 = RT_2)$$

$$W_2 = \frac{R(T_1 - T_2)}{(\gamma - 1)}$$

(iii) Isothermal compression CD. Place the cylinder on the sink at temperature T_2 .

The gas is compressed isothermally till the gas attains the state D. The change is represented by the curve CD. Let the quantity of heat rejected to the sink be Q_2 . This is equal to the work done W_3 on the gas.

$$Q_2 = W_3 = \int_{v_3}^{v_4} P dV = RT_2 \int_{v_3}^{v_4} \frac{dV}{V} = RT_2 \log_e \left(\frac{V_4}{V_3} \right)$$

$$Q_2 = W_3 = -RT_2 \log_e \left(\frac{V_3}{V_4} \right)$$

(iv) Adiabatic compression DA. Place the cylinder on the insulated stand.

The gas is compressed adiabatically until the temperature rises to T_1 . The change is represented by the adiabatic DA.

Work done from D to A is

$$W_4 = \int_{v_4}^{v_1} P dV = -\frac{R(T_1 - T_2)}{(\gamma - 1)}$$

The net work done by the gas

$$W = W_1 + W_2 + W_3 + W_4$$

$$RT_1 \log_e \left(\frac{V_2}{V_1} \right) + \frac{R(T_1 - T_2)}{(\gamma - 1)} + -RT_2 \log_e \left(\frac{V_3}{V_4} \right) - \frac{R(T_1 - T_2)}{(\gamma - 1)}$$

$$W = RT_1 \log_e \left(\frac{V_2}{V_1} \right) - RT_2 \log_e \left(\frac{V_3}{V_4} \right)$$

The points A and D are on the same adiabatic.

$$T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4} \right)^{\gamma-1}$$

The points B and C are on the same adiabatic

$$T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3} \right)^{\gamma-1}$$

From (6) and (7),

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1}$$

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

From (5) and (8),

$$W = RT_1 \log_e \frac{V_2}{V_1} - RT_2 \log_e \frac{V_2}{V_1}$$

$$= R(T_1 - T_2) \log_e \frac{V_2}{V_1}$$

$$W = Q_1 - Q_2 = R(T_1 - T_2) \log_e \frac{V_2}{V_1}$$

The efficiency (η) of the engine is defined as

$$\eta = \frac{\text{Amount of heat converted into work}}{\text{Total heat absorbed from the source}}$$

$$= \frac{Q_1 - Q_2}{Q_1} = \frac{R(T_1 - T_2) \log_e \left(\frac{V_2}{V_1}\right)}{RT_1 \log_e \left(\frac{V_2}{V_1}\right)}$$

Efficiency

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

Carnot's cycles as refrigerator

When the Carnot's engine works as a refrigerator, it absorbs heat Q_2 from the sink at temperature T_2 . W amount of work is done on it by some external means and rejects heat Q_1 to the source at a temperature T_1 (Fig.4.4)

$$\text{Coefficient of performance} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$$

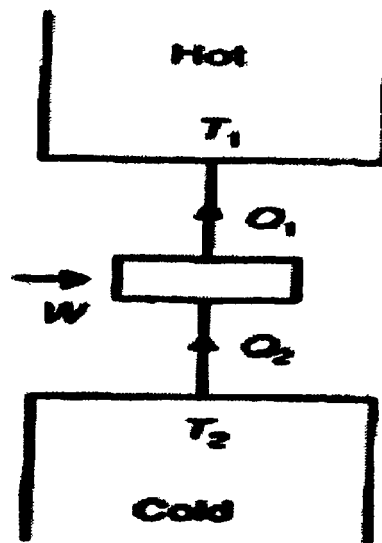


Fig 4.4

The coefficient of performance K is defined as the ratio of the heat taken in from the cold body to the work needed to run the refrigerator.

Check your progress

4. Why any heat engine cannot have 100% efficiency?

Ans:

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.....

4.6 Carnot's theorem

The theorem consists of two parts and can be started as follows:

(i) *All reversible heat engines working between the same two temperatures have the same efficiency whatever be the working substance.*

Explanation. The efficiency of a reversible engine does not depend on the nature of the working substance. The efficiency of a reversible Carnot's engine depends only upon the two temperatures between which it works.

(ii) *Of all the heat engines working between the same two temperature of source and sink, the reversible heat engine has the maximum efficiency possible.*

Explanation. In the case of a Carnot's engines, there is no loss of heat due to friction, conduction or radiation. In a practical engine there is always loss of

energy due to friction, conduction, radiation etc. Hence its efficiency is always lower than that of Carnot's engine. Thus, the Carnot's engine has the maximum efficiency.

Proof. (i) Consider two reversible engines A and B (Fig4.5). They are coupled so that their combination acts as a self acting machine. They work between a source at a higher temperature T_1 and a sink at a lower temperature T_2 . They have different working substances.

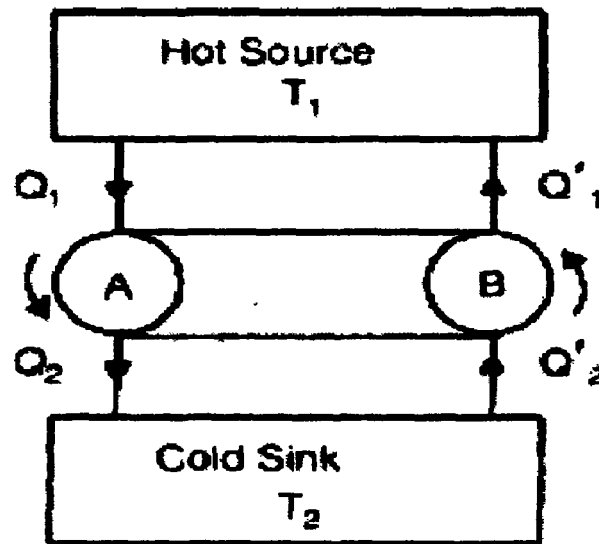


Fig 4.5

Engine A works through a direct cycle. It absorbs an amount of heat Q_1 , at T_1 , and rejects Q_2 at T_2 .

$$\text{Efficiency of engine A} = \eta_A = \frac{Q_1 - Q_2}{Q_1} = \frac{W}{Q_1}$$

Engine B works through the reverse cycle. It absorbs an amount of heat Q'_2 at T_2 and rejects Q'_1 at T_1 .

$$\text{Efficiency of engine B} = \eta_B = \frac{Q'_1 - Q'_2}{Q'_1} = \frac{W}{Q'_1}$$

The useful work done by A equal to $(Q_1 - Q_2)$ can be used to work engine B through the reverse cycle requiring energy $(Q'_1 - Q'_2)$.

Since $Q'_1 - Q'_2 = Q_1 - Q_2$ this system will go on working for ever without any external work being supplied.

Imagine engine A to be more efficient than engine B; i.e., $\eta_A > \eta_B$.

$$\frac{W}{Q_1} > \frac{W}{Q'_1}$$

$$1/Q_1 > 1/Q'_1 \text{ (or) } Q'_1 > Q_1$$

There is a net supply of heat $(Q'_1 - Q_1)$ to the source per cycle which should come from the sink. Since no external work has been done, this is impossible by the second law of thermodynamics. The assumption that $\eta_A > \eta_B$ is wrong.

(ii) Consider an irreversible engine A and a reversible engine B (Fig.4.5). They are coupled such that A works through direct cycle and B works through the reverse cycle. Thus the coupled system acts as self acting machines.

Imagine that $\eta_A > \eta_B$. The fact A is irreversible does not alter any of the argument used above to show that $\eta_A \not> \eta_B$. Therefore, we have proved that irreversible engine cannot be more efficient than a reversible engine when they are working between the same source and sink.

In the case of Carnot's engine, there is no loss of heat due to friction, conduction or radiation. In a practical engine there is always loss of energy due to friction, conduction, radiation etc. Hence its efficiency is always lower than that of Carnot's engine. Thus, the Carnot's engine has the maximum efficiency.

Example 1. An inventor claims to have developed an engine, operating between 800 K and 400 K capable of having an efficiency of 55%. Comment on his claim.

Sol. The efficiency of a Carnot engine operating between 800 K and 400 K is

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{400}{800} = 0.5 = 50\%$$

The efficiency claimed of the newly developed engine = 55%.

Thus the efficiency of the newly developed engine, as claimed by its inventor, is greater than the efficiency of a Carnot's reversible engine operating between the same limits of temperature. But no engine can be more efficient than Carnot's engine working between the same temperatures. Hence the claim of the inventor is not valid.

4.7 Entropy

Definition. *The entropy of a substance is that physical quantity which remains constant when the substance undergoes a reversible adiabatic process.*

Explanation. Consider two adiabatic AF and BE (Fig.4.6) crossed by a number of isothermals at temperatures, T_1, T_2, T_3, \dots . Consider the Carnot cycle ABCD. Let Q_1 be the heat absorbed from A to B at temperature T_1 . Let Q_2 be the heat rejected from C to D at temperature T_2 .

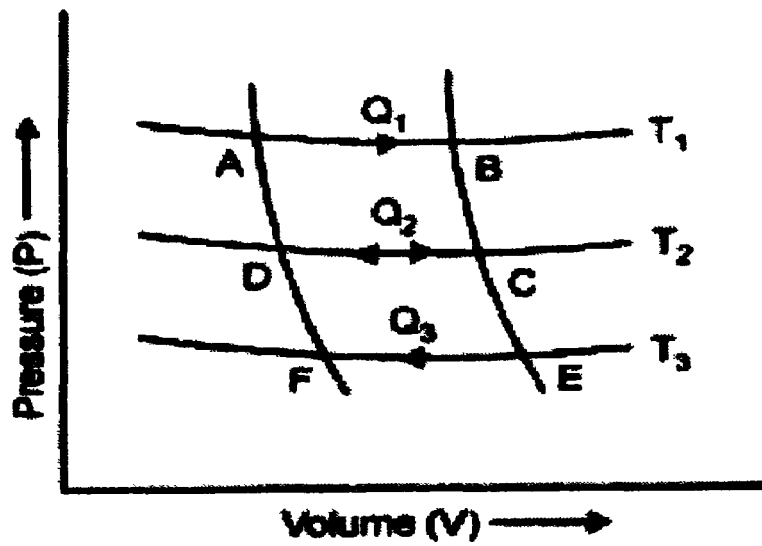


Fig 4.6

Then, from the theory of Carnot engine,

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

Similarly, consider the Carnot cycle DCEF. Q_2 is the heat absorbed at temperature T_2 and Q_3 heat rejected at temperature T_3 . Then,

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_3}$$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \text{constant}$$

Thus, if Q is the amount of heat absorbed or rejected in going from one adiabetic to another along any isothermal at temperature T , then

$$\frac{Q}{T} = \text{constnat}$$

This constant ratio is called the change in entropy in going from the adiabetic AF to the adiabetic BE.

If a system absorbs a quantity of heat dQ at constant temperature T during a reversible process, then entropy increases by

$$dS = \frac{dQ}{T}$$

Similarly, if a substance gives out a quantity of heat dQ at temperature T , during a reversible change, then its entropy decreases by

$$dS = \frac{dQ}{T}$$

Unit of entropy is JK^{-1}

For an adiabatic change, we have $dQ=0$. $dS=0$

Thus, there is no change of entropy during a reversible adiabatic process.

Example: Calculate the change in entropy when 10^{-2} kg of ice at 0°C is converted into water at the same temperature. Given that the specific latent heat of fusion of ice is $3.36 \times 10^5 \text{ J kg}^{-1}$.

Sol. Quantity of heat given to 10^{-2} kg of ice to convert it into water without any change of temperature is

$$dQ = mL = 10^{-2} * (3.36 * 10^5) = 3.36 * 10^3 \text{ J}$$

This process takes place at a constant temperature $T=273 \text{ K}$.

$$\text{Increases in entropy} = dS = \frac{dQ}{T} = \frac{3.36 \times 10^3}{273} = 12.31 \text{ JK}^{-1}$$

Example: Calculate the change in entropy when 5 kg of water at 100°C is converted into steam at the same temperature.

Sol. Heat absorbed by 5 kg of water of 100°C when it is converted into steam at $100^\circ\text{C} = dQ = 5 * (226 \times 10^4) \text{ J} = 1.13 \times 10^7 \text{ J}$.

$$\text{Increases in entropy} = dS = \frac{dQ}{T} = \frac{1.13 \times 10^7}{373} = 30295 \text{ JK}^{-1}$$

Change of entropy in a reversible process (Carnot's cycle)

Consider a reversible Carnot cycle ABCD (Fig.4.7.)

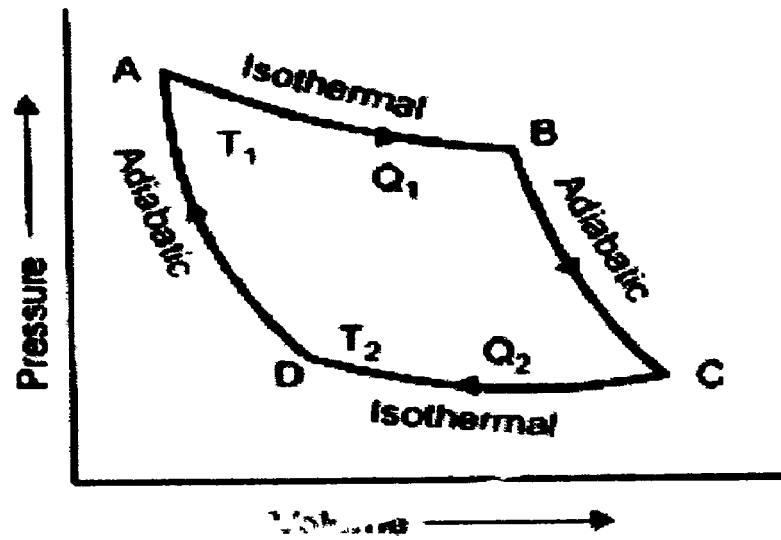


Fig 4.7

- (i) In this isothermal expansion from A to B, the working substance absorbs an amount of heat Q_1 at a constant temperature T_1 .

Increase in entropy of working substance from A to B $= \frac{Q_1}{T_1}$

- (ii) During the adiabatic expansion from B to C, there is no change in entropy.
 (iii) During the isothermal compression from C to D, the working substance gives out a quantity of heat Q_2 at a constant temperature T_2 .

Decrease in entropy of working substance from C to D $= \frac{Q_2}{T_2}$

- (iv) During the adiabatic compression from D to A, there is no change in entropy.

The net change in entropy of the working substance during the cycle ABCE =

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

For a reversible cycle,

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0$$

Thus, the total change of entropy is zero during a Carnot's cycle Entropy change in a reversible cycle is Zero.

Change in entropy in an irreversible process.

Consider an irreversible process like conduction or radiation of heat. Suppose a body at a higher temperature T_1 conducts away a small quantity of heat dQ to another body at a lower temperature T_2 . Then,

$$\text{Decrease in entropy of the hot body} = \frac{dQ}{T_1}$$

$$\text{Increase in entropy of the cold body} = \frac{dQ}{T_2}$$

$$\text{the net increase in the entropy of the system} = dS = \frac{dQ}{T_2} - \frac{dQ}{T_1}$$

dS is always positive since $T_1 > T_2$. Hence there is an increase of entropy. Similarly, there is an increase of entropy during the loss of heat by radiation. Therefore, generally, the entropy of a system increases in all irreversible processes. This is called the law of increase of entropy.

Temperature – entropy diagram

The state of a substance may be represented by points plotted with temperature as ordinates and entropies as abscissa. This is the TS diagram. Here the isothermals are horizontal straight lines (parallel to S-axis). The adiabatics are vertical straight lines (parallel to T-axis)

- (i) From A to B, heat energy Q_1 is absorbed at temperature T_1 . The increase in entropy S_1 takes place from A to B [Fig.4.8]

$$S_1 = \frac{Q_1}{T_1}$$

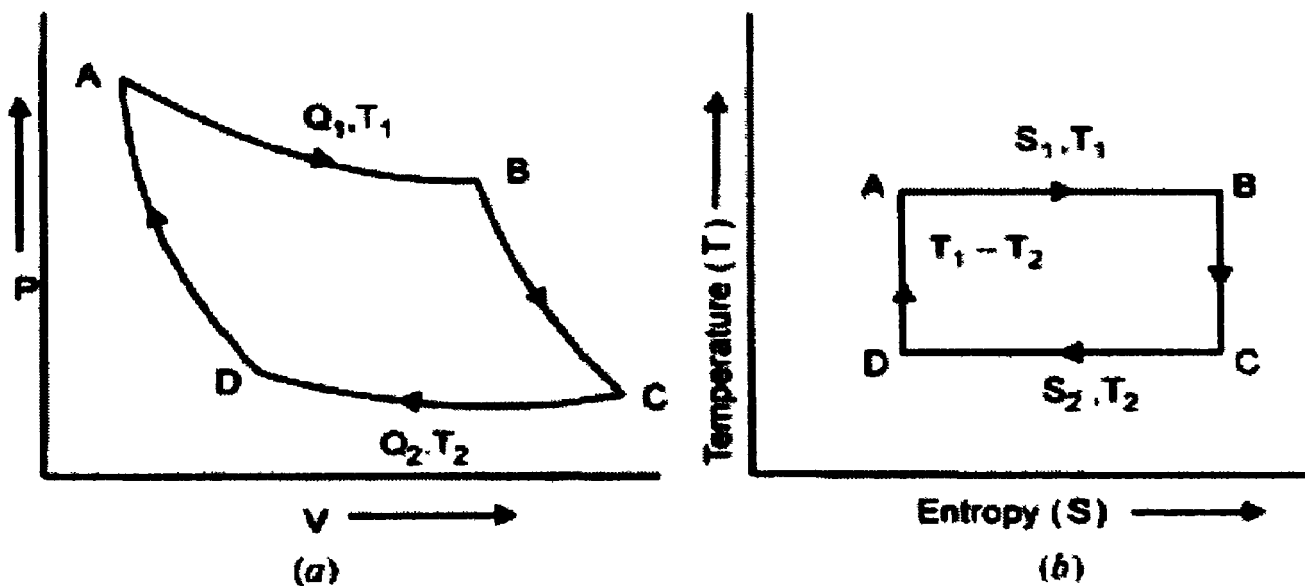


Fig 4.8

- (ii) From B to C there is no change in entropy. Fall of temperature is $T_1 - T_2$.
- (iii) From C to D, there is no decrease in entropy (S_2) at constant temperature T_2 .

$$S_2 = \frac{Q_2}{T_2}$$

- (iv) From D to A, there is no change in entropy but the temperature increases from T_2 to T_1 . The area ABCD in the T-S diagram

$$= S_1(T_1 - T_2) = S_2(T_1 - T_2)$$

$$S_1 = S_2 \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2}$$

$$\text{Area of figure ABCD in T-S diagram} = \frac{Q_1 - Q_2}{T_1 - T_2} (T_1 - T_2) = Q_1 - Q_2$$

The area of ABCD represents the energy converted to work

The efficiency of the engine

$$\eta = \frac{\text{Heat energy converted into work}}{\text{Total heat absorbed}}$$

$$= \frac{S_1(T_1 - T_2)}{T_1 S_1} = \frac{T_1 - T_2}{T_1}$$

Check your progress

5. Why does the entropy of the Universe always tend to increase?

Ans:

.....

.....

Change of entropy in conversion of ice into steam

Let m kg of ice at a temperature T_1 K be converted into water at the same temperature. Then it is heated up to a temperature T_2 K. At T_2 K, it is converted into steam. The net change in entropy from ice to steam can be calculated in 3 steps.

- (i) Let L_1 be the specific latent heat of fusion of ice. To convert m kg of ice at T_1 K into water at the same temperature, an amount of heat $m L_1$ is added to it. Hence

$$\text{Increase in entropy} = \Delta S_1 = \frac{mL_1}{T_1}$$

(ii) Mkg of water at T_1 K is heated to T_2 K

$$\text{Increase in entropy} = \Delta S_2 = \int_{T_2}^{T_1} mC \frac{dT}{T} = mC \log_e \frac{T_2}{T_1}$$

Here, C is the specific heat capacity of water.

(iii) Let L_2 be the specific latent heat of vaporization. When m kg of water at T_2 K is converted into steam at the same temperature, it absorbs heat mL_2 .

$$\text{The Increase in entropy} = \Delta S_3 = \frac{mL_2}{T_2}$$

$$\text{Total gain in entropy} = \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S = \frac{mL_1}{T_1} + mC \log_e \frac{T_2}{T_1} + \frac{mL_2}{T_2}$$

4.8 Third law of thermodynamics

The first and second laws of thermodynamics do not allow the value of the entropy S_0 of a system at absolute zero temperature to be determined. Hence it is impossible to calculate theoretically the absolute values of the entropy. On the basis of a generalization of the experimental investigations of the properties of various substances at very low temperatures, a law was established. This law eliminated the above-mentioned difficulty. It is called the Nernst heat theorem or third law of thermodynamics.

Statement: In any isothermal process carried out at absolute zero temperature, the entropy change of the system equals zero, i.e.

$$\Delta S_{T=0} = 0 \text{ and } S = S_0 = \text{constant.}$$

In other words, at absolute zero temperature, an isothermal process is also isentropic. It follows from the third law of thermodynamics that at $T=0$ K, the heat capacities C_p and C_v and the coefficient of thermal expansion α_1 for any body become zero. This law also leads to the conclusion that it is impossible to accomplish a process as a result of which the temperature of a body is reduced to $T=0$ K i.e.,

It is impossible, by any procedure, no matter up to what extent it is idealized, to bring any impossible to absolute zero temperature in a finite number of operations.

This is the unattainability statement of the third law of thermodynamics. Thus it is experimentally impossible to reach the zero of entropy measuring scale.

Nernst heat theorem is useful in explaining the nature of bodies in the neighbourhood of absolute zero temperature. Its importance lies in the fact that it permits the calculations of absolute values of entropy and the physical interpretation of thermodynamic properties such as Helmholtz and Gibbs free energies etc. It can be conceived that as the temperature of a system tends to absolute zero its entropy tends to a constant which is independent of pressure, and state of aggregation etc. We may put it equal to zero so that the entropy of every substance becomes normalized in an absolute way.

There are several ways of stating the third law.

- (i) **Unattainability statement.** It is impossible by any procedure, no matter up to what extent it is idealized, to bring any system to absolute zero temperature in a finite number of operations.
- (ii) **Nernst statement.** 'no entropy change takes place when pure crystalline solids react at absolute Zero'.
- (iii) **Planck statement.** The entropy of a solid or a liquid is zero at the absolute zero of temperature'.

4.9 Let us sum-up

- **zeroth law of thermodynamics** - *If A and B are in thermal equilibrium with a third body C (the thermometer), then A and B are in thermal equilibrium with each other.*
- **First law of thermodynamics** - *The amount of heat supplied to a system is equal to the algebraic sum of the change in internal energy of the system and the amount of external work done by the system*
- **Second law of Thermodynamics** –
 - (i) **Clausius statement:** It is impossible for self-acting machine, unaided by any external agency, to transfer heat from a body at a lower temperature to a body at a higher temperature, or heat cannot of itself pass from a cold to a hot body.
 - (ii) **Kelvin-Planck statement.** It is impossible to construct a device which, operating in a cycle, has the sole effect of extracting heat from a reservoir and performing an equivalent amount of work.
- Efficiency of Carnot engine is = $\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$
- The entropy of a substance is that physical quantity which remains constant when the substance undergoes a reversible adiabatic process.
- Entropy change in a reversible cycle is Zero.
- The entropy of a system increases in all irreversible processes. This is called the law of increase of entropy.

- **Third law of thermodynamics** - in any isothermal process carried out at absolute zero temperature, the entropy change of the system equals zero, i.e. $S_{T=0} = 0$ and $S = S_0 = \text{constant}$.

4.10 Unit –end exercises

1. Write short notes on : (i) Zeroth law of thermodynamics (ii) Reversible and Irreversible process
2. Explain how first law of thermodynamics leads to the concept of internal energy.
3. Define the efficiency of a heat engine. Obtain an expression for the efficiency of a reversible Carnot's engine with perfect gas as the working substance. Mention the effective ways to increase its efficiency.
4. What is meant by reversible process? Describe Carnot's cycle and show that all reversible engine working between the same two temperatures have the same efficiency. Give two versions of second law of thermodynamics.
5. State and prove Carnot's theorem.
6. Define entropy. Discuss the physical meaning of entropy.
7. Show that during a reversible adiabatic process the entropy of the system remains constant.
8. Derive an expression for the change of entropy of a perfect gas.
9. Obtain an expression for the change of entropy when ice changes into steam.
10. State and explain Third law of thermodynamics.

4.11 Problems for discussion

1. Find the efficiency of the Carnot's engine working between the steam point and the ice point.
2. A Carnot's engine is operated between two reservoirs at temperatures of 450K and 350K. If the engine receives 4200 joules of heat from the source in each cycle, calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine and the work done by the engine in each cycle.
3. A Carnot's engine whose temperature of the source is 400K takes 840 J of heat at this temperature and rejects 630 J of heat to the sink. What is the temperature of the sink? Also calculate the efficiency of the engine.
4. A Carnot's engine working as a refrigerator between 260 K and 300 K receives 2100 J of heat from the reservoir at a lower temperature. Calculate the amount of heat rejected to the reservoir at a higher

temperature. Calculate also the amount of work done in each cycle to operate the refrigerator.

5. Compute the change in entropy when 5 kg of ice at 0°C is converted into steam. Given specific latent heat of fusion of ice to be $3.34 \times 10^5 \text{ J/kg}$ and that of steam to be $226 \times 10^4 \text{ J/kg}$.

4.11 Answers to check your progress & problems for discussion

Check your progress:

1. **Ans:** 100 joules
2. **Ans:** (i) No transfer of heat due to conduction, convection or radiation
(ii) No friction
(iii) Extremely slow isothermal process
3. **Ans:** a) Reversible b) Reversible c) Irreversible d) Irreversible e) Irreversible
4. **Ans:** Efficiency = $\frac{T_1 - T_2}{T_1}$
Efficiency = 100% only if $T_2 = 0\text{K}$. Since 0K is unattainable efficiency cannot be 100%.
5. **Ans:** In the Universe, irreversible processes continuously take place. Hence the entropy always tends to increase.

Answers to Problems for discussion:

1. $T_1 = 100^{\circ}\text{C} = 373\text{K}, T_2 = 0^{\circ}\text{C} = 273\text{K}, \eta = ?$

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{373 - 273}{373} = 0.2681 = 26.81\%$$

2. $T_1 = 450\text{K}; T_2 = 350\text{K}; Q_1 = 4200\text{J}; Q_2 = ?$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$Q_2 = \left(\frac{Q_1}{T_1}\right) T_2 = \frac{4200}{450} * 350 = 3267 \text{ J.}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \left(\frac{350}{450}\right) = 0.2222 = 22.22\%$$

Work done by the engine in each cycle

$$= Q_1 - Q_2 = 4200 - 3267 = 933 \text{ J}$$

3. $Q_1 = 840\text{J}; Q_2 = 630\text{J}; T_1 = 400\text{K}; T_2 = ?$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$T_2 = \left(\frac{T_1}{Q_1}\right) Q_2 = \left(\frac{400}{840}\right) 630 = 300 \text{ K.}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \left(\frac{300}{400}\right) = 0.25$$

% efficiency = 25%

4. $T_1 = 300\text{K}; T_2 = 260\text{K}; Q_2 = 2100\text{J}; Q_1 = ?$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$Q_1 = \left(\frac{T_1}{T_2}\right) Q_2 = \frac{300}{260} * 2100 = 2423 \text{ J.}$$

$$\text{Work done} = w = Q_1 - Q_2 = 2423 - 2100 = 323 \text{ J.}$$

5. The process has three steps: (i) ice changes to water at 273 K. (ii) water is heated from 273 K to 373 K and (iii) water at 373 K changes into steam at 373 K.

$$\Delta S = \frac{mL_1}{T_1} + 2.3026 mC \log_{10} \frac{T_2}{T_1} + \frac{mL_2}{T_2}$$

$$= \frac{5*(3.34*10^5)}{273} + 2.3026 * 5 * 41 + 90 * \log_{10} \frac{373}{273} + \frac{5*(226*10^4)}{373}$$

$$\Delta S = 6117 + 6539 + 30295 = 42951 \text{ JK}^{-1}$$

4.13 Suggested Readings:

1. Thermal physics- R.Murugesan , S.Chand S.Chand & Co, New Delhi..
2. Heat and Thermodynamics -J.B.Rajram and C.L.Arora, S.Chand & Co, New Delhi,2004.
3. Heat, Thermodynamics and Statistical Physics
Brijlal, Dr. N. Subramanyam and P. S. Hemne.

Revised edition, Reprint 2012 S.Chand& Company Ltd., New Delhi

- 4. Thermodynamics and Statistical Physics**
Singhal, Agarwal, SathyaPrakash
12th edition, 2008, PragatiPrakashan, Meerut
- 5. Thermodynamics, Statistical thermodynamics and Kinetics**
Thomas Engal, Philip Reid
1st edition, 2007, Dorling Kindersley (India) Pvt Ltd, New Delhi.

UNIT 5

Structure:

- 5.1. Introduction
- 5.2. Objectives
- 5.3. Probability
- 5.4. Phase space & elements of phase space
- 5.5. Micro state and Macro states
- 5.6. Fundamental postulates of statistical mechanics
- 5.7. Entropy and probability
- 5.8. Maxwell –Boltzmann statistics
- 5.9. Quantum statistics
- 5.10. Bose - Einstein statistics
- 5.11. Fermi – Dirac statistics
- 5.12. Let us sum up.
- 5.13. Unit - end Exercises
- 5.14. Problems for discussion
- 5.15. Answer for check your progress
- 5.16. Suggested Readings.

5.1. Introduction:

A study of thermodynamics gives us various macroscopic properties that are related through an equation of state having only two independent parameters. However, the equation of state cannot be deduced from the laws of thermodynamics. It has to be obtained experimentally. The ordinary laws of mechanics were the only tool to explain physical phenomena, up to the end of 17th century. In certain cases, particularly where the system contains a large number of particles, ordinary laws of mechanics could not be used, as it is impossible to follow the motion of each particle. For example, a point of matter contains a very large number of atoms or molecules. (Avogadro's number $N_0 = 6 \times 10^{26}$ per kg mole). Therefore, it is impossible to apply the ordinary laws of mechanics to a physical system containing large number of particles, particularly that of electrons. Such problems are however, successfully solved by statistical mechanics. The larger is the number of particles in the physical system considered, the more nearly correct are the statistical predictions. Smaller the number of particles in a mechanical system, the statistical mechanics goes on becoming meaningless. Before the advent of quantum theory, Maxwell, Boltzmann, Gibbs etc. applied the statistical method making the use of classical physics. These methods are known as classical statistics or Maxwell-Boltzmann statistics. In this unit we are going to see about both classical & quantum statistics.

5.2. Objectives:

After going through this unit, you should be able to

- understand the significance of the terms probability, phase space, microstate and macro states.
- define thermodynamic probability
- derive the relation between entropy and thermodynamic probability
- understand the postulates of statistical mechanics
- derive the distribution functions for systems obey Maxwell – Boltzmann statistics, Fermi – Dirac statistics & Bose - Einstein statistics.

5.3 Probability:

The probability of an event may be defined as the ratio of the number of cases in which the event occurs to the total number of cases.

Thus, the Probability of an event =

$$\frac{\text{Number of cases in which the even occurs}}{\text{total number of cases}} \quad \dots\dots (5.1)$$

Suppose an event can happen in a ways and fails to happen in b ways, then the probability of happening the event = $\frac{a}{a+b}$. Hence $(a+b)$ represents the total number of equally likely possible ways. It should be noted that the sum of these two probabilities is always 1; since the event must either occur or fail.

To evaluate the probability of random event, we consider a unit of measurement. An event is called a 'sure' event if it occurs in an experiment. Thus, the probability of a 'sure' event is assumed to be equal to 1 and that of an impossible event to be equal to zero. Thus, the probability P of a random event lies between 0 and 1 i.e.,

$$0 \leq P \leq 1 \quad \dots\dots\dots (5.2)$$

This is further explained by the following experiments:

1. **Throwing a coin:** Suppose we toss a coin. Either the 'head' can come upward or the 'tail' i.e., an event can occur in a total number of two equally likely ways. The number of ways in which the 'head' can come up is only one. Therefore, the probability that the 'head' may come up is $\frac{1}{2}$. Similarly, the probability that the 'tail' may come up is also $\frac{1}{2}$.
2. **Throwing a die:** A die is a homogeneous, regular and balanced cube with six faces marked numbers of dots from 1 to 6 engraved on them. It is supposed that the die is symmetrical and cannot fall of its edges. When

the die is thrown it falls one of its faces upward i.e., yields one of the six results and no other. All outcomes are equally likely in a single throw of dice. Out of six possible results only one is favourable for the appearance of six spots. In other words, the probability of any one face (say with a number 3) to come up is $1/6$. The set of all possible outcomes can be written as $S(1, 2, 3, 4, 5, 6)$. The probability of the die coming up with an even number is $3/6$ as there are only three even numbers on the die 2, 4 and 6.

$$P(\text{even}) = 3/6 = 1/2$$

Likewise, the probability of the die coming up with odd number is $3/6$ or $1/2$.

The probability of the die coming up with any number less than 6 is given by

$$P(\text{a number} < 6) = 5/6$$

As there are five numbers 1, 2, 3, 4, 5 which are less than 6.

Zero Probability: If we want to know the probability of the die coming up with face marked with a number 7. The die has only six faces marked serially from 1 to 6. There is no face marked as 7. Therefore, probability of appearing a number 7 is zero, i.e.

$$P(\text{number } 7) = 0/6 = 0$$

In other words, impossible event is always zero.

Probability one: The probability of appearing any number less than 7 is one. This is because all the six faces of the die are marked from 1 to 6, i.e., the numbers less than 7.

$$P(\text{number} < 7) = 6/6 = 1$$

Total probability: If a is the number of cases in which an event occurs and b the number of cases in which an event fails, then

Probability of occurrence the event = $\frac{a}{a+b}$ and

Probability of failing the event = $\frac{b}{a+b}$

The sum i.e., the total probability is always one, since the event ,may either occur or fail.

Principle of equal A priori probability:

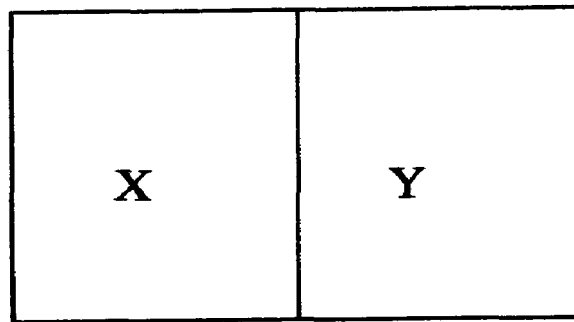


Fig : 5.1

Suppose we toss a coin it is clear in mind that the coin will fall either with its 'head' up or 'tail' up. Similarly if a six faced cubical dice is thrown, it is sure that the dice will fall with one of its six faces upward. In the same way, if we have an open box divided into two equal sized compartments X and Y as shown in fig 5.1 and a small particle is thrown from a large distance in such a way that it must fall in either of the two compartments, then the probability of the particle to fall in the compartment marked X is equal to the probability that it may fall into the compartment marked Y. Again there is an equal probability.

This principle of assuming equal probability for events which are equally likely to occur is known as the principle of equal a priori probability.

Apriori means something which exists in our mind prior to and independently of the observations we are going to make.

This principle of equal apriori probability will not hold good, if in the above example, the two compartments are of unequal size.

Probability and Frequency:

All the possible outcomes, in the examples discussed above, are assumed to be known. This is not always possible in practice and hence formula given by equation (5.1) is not a general formula. It can be used only in experiments that possess symmetry. Suppose, the die is asymmetric by adding a little load (by wax) to one of its faces. Now all the outcomes are not equally likely and we cannot say that the probability at appearance of six spots is $1/6$. For all such cases, we adopt a technique as under.

Suppose we toss a coin, say N times and we find that 'Head' appears M times. Here we introduce a term frequency of an event F as

$$F = \frac{\text{No. of trials in which } A \text{ occurs}}{\text{Total number of trials}} = \frac{M}{N} \dots\dots\dots(5.3)$$

Thus, if a coin is tossed 50 times and in 10 of them the coin shows Heads, the frequency of this event is $\frac{10}{50} = 0.2$. From the classical definitions of probability, the probability of occurrence of 'Head' is 0.5 or 50%. Hence, we conclude that frequency is not the same as probability. There must be a relationship between frequency and probability. As the number of trials is increased, the frequency of the event progressively tends to stabilize and gradually approaches a constant value, known as the probability of the event. We define probability in terms of frequency as

$$P = \lim_{n \rightarrow \infty} \frac{M}{N} \dots\dots\dots(5.4)$$

Thus, in order to obtain sufficiently accurate result, trials must be conducted until the ratios $\frac{M}{N}$ differ from one another by a very small value.

Basic rules of probability:

Additive Law of Probability:

This is applicable to mutually exclusive events. Two or more events are said to be mutually exclusive if the occurrence of any one of them prevents the occurrence of others. Such events never occurs simultaneously.

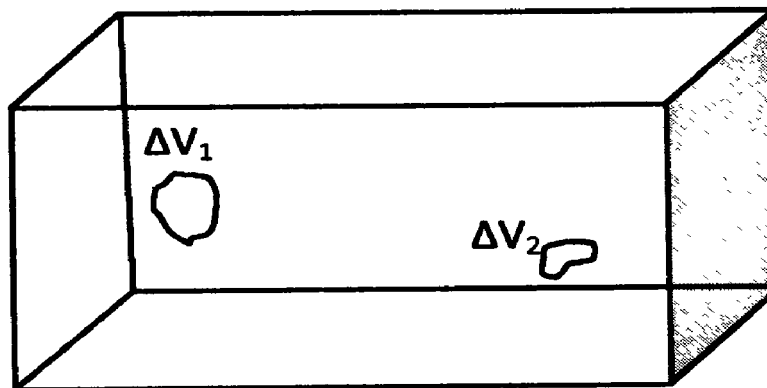


Fig 5.2

Consider two small non-overlapping region ΔV_1 and ΔV_2 in a box of volume as shown in fig. (5.2) A particle in ΔV_1 rules out the possibility of its being present, at the same instant in ΔV_2 and vice versa. The two events, thus, are mutually exclusive.

Suppose in N trials the particle is found m_1 times in ΔV_1 and m_2 times in ΔV_2 . The probabilities of finding particles in the two regions are

$$p_1 = \frac{m_1}{N} \text{ and } p_2 = \frac{m_2}{N} \text{ respectively.}$$

The number of times that the particle will be found at least one of the two regions in N trials is $(m_1 + m_2)$. Hence, the probability will be

$$P(\Delta V_1 \text{ or } \Delta V_2) = \frac{m_1 + m_2}{N} = \frac{m_1}{N} + \frac{m_2}{N} = p_1 + p_2$$

This law can be generalized to any number of mutually exclusive events, giving probabilities, say, $p_1, p_2, p_3, \dots, p_N$, then the probability that any one of them occurs is the sum of the probability of these events, i.e.,

$$P = p_1 + p_2 + p_3 + \dots + p_N = \sum_{i=1}^N p_i$$

This is known as additive law of probability.

Multiplication Rule: Probability

In the calculations of probabilities, we sometimes come across random events; such that the probability of occurrence of one does not affect the probability of occurrence of the other. For example in fig. 5.2, the probability that a molecule A gets into ΔV_1 , at a particular instant is $p_1 = \frac{\Delta V_1}{V}$. The probability that another molecule gets into volume ΔV_2 at the same instant is $p_2 = \frac{\Delta V_2}{V}$, regardless of whether or not the molecule A gets into ΔV_1 . We want to calculate the probability of joint occurrence of these events, i.e., the probability of A getting into ΔV_1 and B getting into ΔV_2 at the same instant. Suppose in N trials, the molecule A is found m times in ΔV_1 . If p_2 is the probability that B gets into ΔV_2 , irrespective of the presence of A in ΔV_1 , the number of times the two events will occur simultaneously in mp_2 . Thus, the joint probability of occurrence of these two events, is

$$P = \frac{mp_2}{N}$$

$$= \frac{m}{N} \times p_2$$

$$P = p_1 \times p_2 \quad \left(p_1 = \frac{m}{N} \right)$$

Thus, probability of joint occurrence of two independent events is equal to the product of the probabilities of each of these independent events.

5.4. Phase Space & Elements of Phase Space:

To specify the position as well as energy of a molecule inside a gas, we must specify three space coordinates x, y, z and three momentum coordinates p_x, p_y, p_z . As a purely mathematical concept, we may imagine six dimensional space in which coordinates are x, y, z, p_x, p_y, p_z . This six dimensional space for a single molecule is called phase space or μ - space. The instantaneous state of a particle in the phase space is represented by a point known as phase point or representative point. In phase space we may consider an element of volume $dx, dy, dz, dp_x, dp_y, dp_z$. Any such element of volume in six dimensional space is called a cell. Thus the phase space may be divided into a large number of cells. A cell may contain a large number of phase points.

In classical or Maxwell – Boltzmann statistics, there is no restriction on the volume of the phase cell. The volume of the phase cell may be very small tending to zero also.

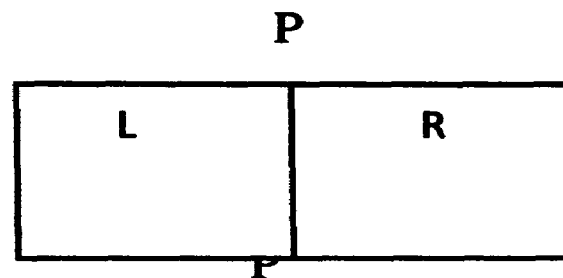
In quantum statistics, the volume of the phase cell

$$V = \Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z = h^3$$

Here, h is Planck's constant.

5.5 Microstate and Macro states:

Consider the distribution of 4 particles in two halves of a box



Draw an imaginary line PP' to make two equal portions L and R of the box.

Let the four identical particles be designated by a, b, c and d. The possible distribution of these particles in the box is

- (i) 4 particles in L and 0 in R halves
- (ii) 3 particles in L and 1 in R halves
- (iii) 2 particles in L and 2 in R halves
- (iv) 1 particles in L and 3 in R halves
- (v) 0 particles in L and 4 in R halves

For brevity we call the above distributions of the particles in the box as (4, 0), (3, 1), (2, 2), (1, 3) and (0, 4) respectively.

1. Now, the distribution (4, 0) can occur in only one way i.e., a, b, c, d all in L and no particle in R halves.
2. The distribution (3,1) can occur in four ways
3. The distribution (2, 2) occurs in 6 ways
4. The distribution (1, 3) occurs in 4 ways
5. The distribution (0, 4) occurs in 1 way.

Left (L)	Right (R)
abc	d
abd	c
acd	b
bcd	a

Table 1

Thus, the total number of ways in which four identical particles a, b, c, d can occupy two halves of the box are $1 + 4 + 6 + 4 + 1 = 16$, corresponding to 5 different distributions.

There are 5 macro – states and 16 micro states.

Corresponding to macro – state (3, 1) there are 4 micro – states and corresponding to macro – state (2, 2) there are 6 micro – states and so on.

5.6 Fundamental postulates of Statistical Mechanics:

1. Any gas may be considered to be composed of molecules that are in motion and behave like very small elastic spheres.
2. All the cells in the phase space are of equal size.
3. All accessible microstates corresponding to possible macro states are equally probable. This is called the *postulate of equal a priori probability*.
4. The equilibrium state of a gas corresponds to the macrostate of maximum probability.
5. The total number of molecules is constant.

5.7 Entropy and probability:

5.7.1 Thermodynamic Probability

The thermodynamic probability of a particular macrostate is defined as the number of microstates corresponding to that macrostate.

It is represented by W

Consider two cells in phase space represented by i and j and four molecules a,b, c and d. Let N_i and N_j be the number of molecules in the cells i and j respectively. Then the possible macrostates are five in number (fig. 5.2)

N_i	4	3	2	1	0
N_j	0	1	2	3	4

Fig 5.2

In general, to each of these five macrostates there correspond a different number of microstates. Let us consider the microstates corresponding to the macrostate $N_i = 3$, and $N_j = 1$. The number of microstates corresponding to the macrostate $N_i = 3, N_j = 1$ is four, as shown in fig 5.3.

Therefore, the thermodynamic probability for the macrostate, $N_i = 3, N_j = 1$ is 4. That is $W = 4$.

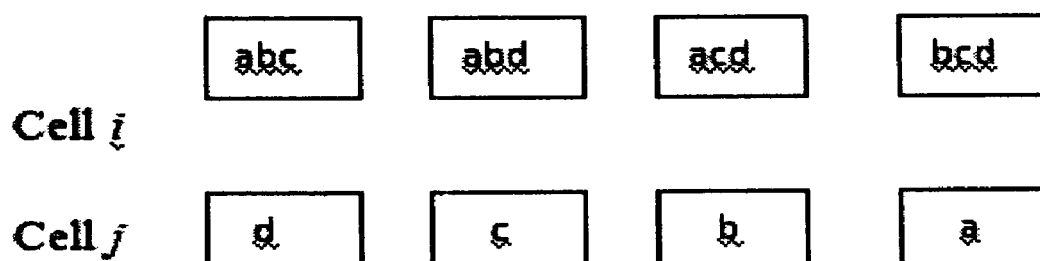


Fig. 5.3

A *macrostate* is specified by just giving the number of molecules in each cell of phase space.

For defining a *microstate* we should specify to which cell each molecule of the system belongs at a particular instant.

5.7.2 Boltzmann's Theorem on Entropy and Probability:

Boltzmann discovered a relation between entropy (a thermodynamical quantity) and probability (a statistical quantity). Boltzmann started from a simple idea that the equilibrium state of the system is the state of maximum probability. That is, the probability of the system in equilibrium state is maximum. But from the thermodynamic point of view, the equilibrium state of the system is the state of maximum entropy. If the system is not in equilibrium, then changes take place within the system until the equilibrium state or the state of maximum entropy is reached. Thus, in equilibrium state both the entropy and thermodynamical probability has their maximum values. As equilibrium state is the state of maximum entropy and maximum probability, Boltzmann concluded that entropy is a function of probability. That is,

$$S = f(w) \dots\dots\dots (1)$$

Here, S is entropy and W is the thermodynamical probability of the state.

Let us consider two separate systems having entropies S_1 and S_2 and thermodynamic probabilities W_1 and W_2 .

Then $S_1 = f(W_1)$ and $S_2 = f(W_2) \dots\dots\dots (2)$

The total entropy of the two systems is

$$S_1 + S_2 = f(W_1) + f(W_2) \dots\dots\dots(3)$$

But the thermodynamic probability of the two systems taken together is $W_1 W_2$.

$$f(W_1 W_2) = f(W_1) + f(W_2) = S_1 + S_2 \dots\dots\dots(4)$$

If this relation is to be satisfied, $f(W)$ must be a logarithmic function of W

$$f(W) = k \log W$$

$$S = k \log W \dots\dots\dots (5)$$

To Derive the Boltzmann Relation Connecting Entropy and Probability

The entropy of any thermo dynamical system always tends to have a maximum value. The thermodynamic probability of a system is also a maximum at equilibrium. So Boltzmann thought that a relation could exist between entropy (S) and probability (W). According to this , S is a function W.

$$S = f(W) \dots\dots\dots(1)$$

Consider two separate systems with entropies S1 and S2 and thermodynamic probabilities W1 and W2 respectively.

$$S_1 = f(W_1) \text{ and } S_2 = f(W_2) \dots\dots\dots(2)$$

The total entropy of the two systems is

$$S = S_1 + S_2 = f(W_1) + f(W_2) \dots\dots\dots(3)$$

But the thermodynamic probability of the two systems taken together is $W_1 W_2$.

$$S = f(W_1 W_2) \dots\dots\dots(4)$$

From Eqns. (3) and (4), we have

$$f(W_1 W_2) = f(W_1) + f(W_2) \dots\dots\dots(5)$$

Differentiating Eq. (5) partially with respect to W1, to get

$$W_2 f'(W_1 W_2) = f'(W_1) \dots\dots(6)$$

Differentiating Eq. (5) partially with respect to W2, we get

$$W_1 f'(W_1 W_2) = f'(W_2) \dots\dots(7)$$

Dividing Eq. (6) by Eq. (7), we get,

$$\frac{f'(W_1)}{f'(W_2)} = \frac{W_2}{W_1}$$

i.e., $W_1 f'(W_1) = W_2 f'(W_2) = k.$

Here, k is any constant.

$$f'(W_1) = \frac{k}{W_1} \text{ and } f'(W_2) = \frac{k}{W_2}$$

Integrating we get,

$$f(W_1) = k \log W_1 + C_1$$

$$f(W_2) = k \log W_2 + C_2$$

In general we may write

$$f(W) = k \log W + C$$

$$S = k \log W + C, \quad \dots\dots\dots(8)$$

The constant of integration C in above equation is chosen in accordance with the *third law of thermodynamics also known as Nernst heat theorem*.

According to this theorem, the entropy of a thermo dynamical system tends to zero as its temperature tends to absolute zero. The temperatures approaching absolute zero are generally attained by the process of adiabatic demagnetization. The process requires to subject the paramagnetic salts to high magnetic field so that the spins of the electrons align themselves parallel to the direction of the applied field. At absolute zero all the electron spins are aligned parallel to the direction of the field since at absolute zero there is no thermal energy to disturb their alignment. Thus at absolute zero there is only one configuration where all the electron spins are ordered in a particular direction, i.e., at absolute zero, the thermo dynamical probability (or weight of configuration) is 1. Hence, for a thermo dynamical system at absolute zero, $W = 1$ and $S = 0$.

From Eq. (8), we get $C = 0$

$$S = k \log W \quad \dots\dots\dots(9)$$

5.8 Maxwell – Boltzmann statistics:

5.8.1 Statistical equilibrium:

Boltzmann canonical principle is applied to determine the equilibrium state of the system. According to this principle, *Equilibrium state of a system is that which is most probable*.

Consider an isolated system composed of a large number of N of particles, in which each particle has available to it several states with energies E_1, E_2, E_3, \dots . At a particular time the particles are distributed among the different states, so that n_1 particles have energy E_1 ; n_2 particles have energy E_2 ; and so on.

The total number of particles is

$$N = n_1 + n_2 + n_3 + \dots = \sum_i n_i \quad \dots\dots\dots(1)$$

We assume that the total number of particles remains constant for all processes occurring in the system

The total energy of the system is

$$E = n_1 E_1 + n_2 E_2 + \dots = \sum_i n_i E_i \quad \dots\dots\dots(2)$$

If the system is isolated, the total energy E must be constant. However, as a result of their mutual interactions and collisions, the distribution of the particles among the available energy states may be changing.

For example in a gas, a fast molecule may collide with a slow one; after the collision, the fast molecule may have slowed down and the slow one may have speed up. Or an excited atom may collide in - elastically with another atom, with a transfer of its excitation energy into kinetic energy of both atoms. Hence, in both examples, the particles after the collision are in different states. In other words, the numbers n_1, n_2, n_3, \dots which give the distribution of the N particles among the available energy states, may be changing. It is reasonable to assume that for each macroscopic state of a system of particles there is a distribution which is more favoured than any other. In other words, we may say that *given the physical conditions of the system of particles, there is a most probable distribution*. When this distribution is achieved, the system is said to be in *statistical equilibrium*

5.8.2 Derivation of Maxwell – Boltzmann Distribution Law:

Consider a system of N distinguishable molecules of a gas. Suppose n_1 of them have energy E_1 , n_2 have energy E_2 n_i have energy E_i and so on. Thus the entire assembly can be divided into different energy states with energies $E_1, E_2, E_3, \dots, E_i$ and having $n_1, n_2, n_3, \dots, n_i$ molecules.

(1) The total number of molecules N is constant. Hence

$$N = n_1 + n_2 + n_3 + \dots + n_i + \dots = \text{constant}$$

$$\delta N = \delta n_1 + \delta n_2 + \delta n_3 + \dots + \delta n_i + \dots = 0$$

$$\text{i.e., } \sum_i \delta n_i = 0$$

(2) The total energy E of the gas molecules is constant. Hence

$$E = E_1 n_1 + E_2 n_2 + E_3 n_3 + \dots + E_i n_i + \dots = \text{constant}$$

$$\sum_i E_i \delta n_i = 0$$

(3) Suppose there are g_i cells with the energy E_i . The total number of ways in which n_i molecules can have energy E_i is $(g_i)^{n_i}$. Hence the total number of ways in which N molecules can be distributed among the various energies is

$$W_1 = (g_1)^{n_1} (g_2)^{n_2} (g_3)^{n_3} \dots \dots (g_i)^{n_i} \dots$$

The number of ways in which groups of $n_1, n_2, n_3, \dots, n_i$ particles can be chosen from N particles is given by

$$W_2 = \frac{N!}{n_1!n_2!n_3!\dots\dots}$$

The number of distinguishable ways in which N molecules can be distributed among the possible energy levels is

$$W = W_1 W_2 = \frac{N!}{n_1!n_2!n_3!\dots\dots} (g_1)^{n_1} (g_2)^{n_2} (g_3)^{n_3} \dots \dots (g_i)^{n_i} \dots (3)$$

The quantity W is called the *thermodynamic probability* for the system.

For the most probable distribution, W is maximum subject to the restriction that the total number of particles N and the total energy E are constant.

The natural logarithm of Eq. (3) is

$$\ln W = \ln N! - \sum \ln n_i! + \sum n_i \ln g_i$$

By Stirling's theorem, $\ln n! = n \ln n - n$

$$\ln W = (N \ln N - N) - (\sum n_i \ln n_i + \sum n_i) + \sum n_i \ln g_i$$

$$\ln W = N \ln N - \sum n_i \ln n_i + \sum n_i \ln g_i \dots \dots (4)$$

From Eq. (4), we have for maximum W

$$\delta \ln W_{max} = -\sum n_i \frac{1}{n_i} \delta n_i - \sum (\ln n_i) \delta n_i + \sum (\ln g_i) \delta n_i = 0$$

$$-\sum n_i \frac{1}{n_i} \delta n_i + \sum (\ln g_i) \delta n_i = 0 \quad [\sum \delta n_i = 0] \dots (5)$$

Eqs. (1) and (2) can be incorporated into eq. (5) by making use of Lagrange's method of undetermined multipliers.

Multiplying Eq. (1) by $-\alpha$ and Eq. (2) by $-\beta$ and adding to Eq. (5), we get

$$\sum(-\ln n_i + \ln g_i - \alpha - \beta E_i)\delta n_i = 0 \quad \dots(6)$$

$$(-\ln n_i + \ln g_i - \alpha - \beta E_i) = 0$$

$$n_i = g_i e^{-\alpha} e^{-\beta E_i} \quad \dots\dots(7)$$

Eq. (7) is called Maxwell – Boltzmann distribution law.

M – B Distribution in terms of temperature

It can be shown that $\beta = 1/kT$ where $k =$ Boltzmann's constant and $T =$ absolute temperature of the gas.

$$n_i = g_i e^{-\alpha} e^{-E_i/kT} \quad \dots\dots(8)$$

5.8.3 Applications of Maxwell – Boltzmann Distribution law to an Ideal gas

Molecular Energies in an Ideal Gas:

The M.B distribution law is

$$n_i = g_i e^{-\alpha} e^{-E_i/kT} \quad \dots\dots\dots(1)$$

Consider an ideal gas that contains N molecules. Consider a continuous distribution of molecular energies instead of the discrete set, E_1, E_2, E_3, \dots . Then Eq. (1) becomes

$$n(E)dE = g(E)e^{-\alpha} e^{-E_i/kT} dE \quad \dots\dots\dots(2)$$

Here, $n(E) dE$ represents the number of molecules having energies between E and $E+ dE$.

$g(E) dE$ represents the number of states that have energies between E and $E + dE$

Let us find $g(E) dE$.

A molecule of energy E has a momentum p whose magnitude is

$$p = \sqrt{2mE} = \sqrt{p_x^2 + p_y^2 + p_z^2} \quad \dots\dots\dots(3)$$

Each set of momentum components p_x, p_y, p_z specifies a different state of motion. Let us imagine a momentum space whose coordinate axes are p_x, p_y, p_z (fig. 5.4). The number of momentum states available to a particle with a momentum whose

magnitude is between p and $p + dp$ is proportional to the volume of a spherical shell in momentum space of radius p and thickness dp .

Volume of this spherical shell is $4\pi p^2 dp$

$$\text{Hence, } g(p)dp = Bp^2 dp \dots\dots\dots(4)$$

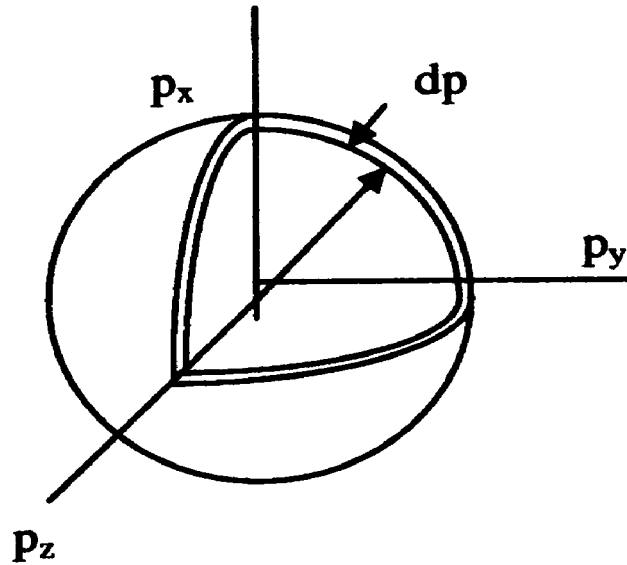


fig: 5.4

Since each momentum magnitude p corresponds to a single energy E , the number of energy states $g(E) dE$ between E and $E + dE$ is the same as the number of momentum states $g(p) dp$ between p and $p + dp$.

$$g(E) dE = Bp^2 dp \dots\dots\dots(5)$$

But $p^2 = 2mE$ and $dp = \frac{m dE}{\sqrt{2mE}}$

$$g(E) dE = \sqrt{2} m^{3/2} B \sqrt{E} dE$$

Substituting for $g(E) dE$ in Eq . (2),

$$n(E)dE = C \sqrt{E} e^{-(E/kT)} dE \dots\dots\dots(7)$$

Here $C = \sqrt{2} m^{3/2} B e^{-\alpha} = \text{constant}$

To find C we make use of the normalization condition that the total number of molecules is N . Therefore,

$$N = \int_0^\infty n(E)dE = C \int_0^\infty \sqrt{E} e^{-(\frac{E}{kT})} dE \dots\dots\dots(8)$$

From a table of definite integrals we find that

$$\int_0^{\infty} \sqrt{x} e^{-ax} dx = \frac{1}{2a} \sqrt{\frac{\pi}{a}}$$

$$N = C \frac{1}{2(1/kT)} \sqrt{\frac{\pi}{(1/kT)}} = C \times \frac{\sqrt{\pi}}{2} \times (kT)^{3/2}$$

$$C = \frac{2\pi N}{(\pi kT)^{3/2}} \dots\dots\dots(9)$$

$$n(E) dE = \frac{2\pi N}{(\pi kT)^{3/2}} \sqrt{E} e^{-E/kT} dE \dots\dots\dots(10)$$

Eq. (10) is plotted in fig. 5.4 in terms of kT.

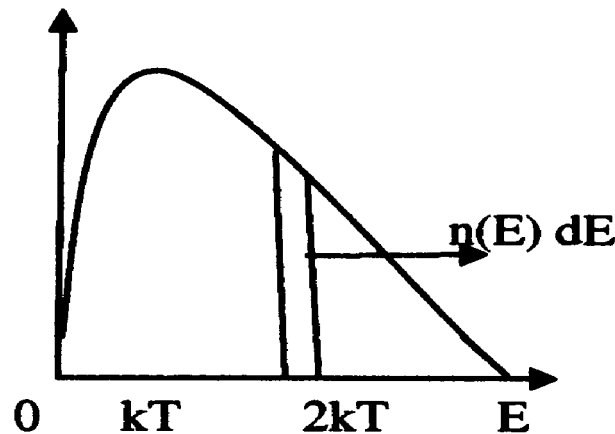


Fig. 5.5

The total internal energy of the system is

$$E = \int_0^{\infty} E n(E) dE = \frac{2\pi N}{(\pi kT)^{3/2}} \int_0^{\infty} E^{3/2} e^{-(E/kT)} dE$$

The value of the definite integral is $\frac{3}{4} (kT)^2 \sqrt{\pi kT}$

$$E = \frac{2\pi N}{(\pi kT)^{3/2}} \times \frac{3}{4} (kT)^2 \sqrt{\pi kT} = \frac{3}{2} NkT \dots\dots\dots(11)$$

The average energy of an ideal gas molecule is E/N.

$$\bar{E} = \frac{3}{2} kT \dots\dots\dots(12)$$

Maxwell – Boltzmann velocity distribution law

Substitute $E = (1/2)mv^2$ and $dE = mv dv$ in Eq. (10). Thus we get

$$n(v)dv = \frac{\sqrt{2} \pi N m^{1/2}}{(\pi kT)^{1/2}} v^2 e^{-mv^2/2kT} dv \dots\dots\dots(13)$$

This equation represents the number of molecules with speeds between v and $v + dv$ in an assembly of ideal gas containing N molecules at absolute temperature T . This formula is plotted in fig. 5.5

5.9. Quantum Statistics:

Statistical mechanics can be divided into two main classes.

1. Classical Statistics or Maxwell – Boltzmann statistics
2. Quantum Statistics

Classical statistics interpreted successfully many ordinarily observed phenomena such as temperature, pressure, energy etc. But it failed to account for several other experimentally observed phenomena such as black body radiation, photoelectric effect, specific heat capacity at low temperatures etc. This failure of classical statistics forced the issue in favour of the new quantum idea of discrete exchange of energy between systems. Thus, a new quantum statistics was investigated. There are two types of quantum statistics.

1. Bose – Einstein statistics
2. Fermi – Dirac statistics

1. Bose – Einstein Statistics:

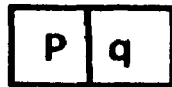
This is applicable to the identical, indistinguishable particles of zero or integral spin. These particles are called *bosons*. The examples of bosons are helium atoms at low temperature and the photons.

2. Fermi – Dirac Statistics:

This is applicable to the identical, indistinguishable particles of half – spin. These particles obey Pauli exclusion principle and are called *fermions*. The examples of fermions are electrons, protons, neutrons etc. In such systems of particles, no more than one particle can be in one quantum state.

The essential difference between the three statistics may be illustrated in the following simple manner. Let there be only two particles of a collection and only two cells to be occupied. Then fig. 5.7 illustrates the essential differences between the three statistics.

Classical statistics:



Bose- Einstein statistics:



Fermi – Dirac statistics



Consider an isolated system composed of a large number of particles in which each particle has available to it several states with energies E_1, E_2, E_3, \dots . At a particular time the particles are distributed among the different states, so that n_1 particles have energy E_1 ; n_2 particles have energy E_2 ; and so on.

The total number of particles is

$$N = n_1 + n_2 + n_3 + \dots = \sum_i n_i \quad \dots\dots\dots(1)$$

We assume that the total number of particles remains constant for all processes occurring in the system.

The total energy of the system is

$$E = n_1 E_1 + n_2 E_2 + \dots = \sum_i n_i E_i \quad \dots\dots\dots(2)$$

If the system is isolated, the total energy E must be constant. According to the basic postulate of statistical mechanics, the greater the number W of different ways in which the particles can be arranged among the available states to yield a particular distribution of energies, the more probable is the distribution. It is assumed that each state of certain energy is equally likely to be occupied.

Therefore, the procedure, for determining the most probable statistical distribution involves two steps: (i) obtaining the number of distinguishable arrangements (W) which give rise to the same distribution, and (ii) maximizing this number of arrangements (W) with respect to different distributions.

Quantum Statistics of Identical Particles:

Identical particles:

Identical particles in a system are regarded as those particles which when interchanged in the system will not make any change in it.

Quantum statistics is based on the following assumptions:

1. The smallest particles of a system are not molecules or atoms but particles like electrons, neutrons, α - particles, photons (electromagnetic radiation), phonons, etc. These quantum particles do not follow the common Newtonian laws of motion but are governed by Einstein's relativistic mechanics.
2. The coordinates of the quantum particles can not be measured with perfection. There are limits to the minimum values of space coordinates dq and momentum coordinates dp below which no measurement can be done.

According to Heisenberg's Uncertainty principle, for any i th quantum particle, the measured values of space and momentum coordinates should follow

$$dq_i dp_i \geq \frac{1}{2}h$$

Here, h is the Planck's constant.

3. The quantum particles of one type are all identical and indistinguishable from each other.

Types of Quantum particles:

The quantum particles are divided into two distinctly different types.

They are

- (i) The particles whose spin angular momentum are integral multiples of \hbar are called the **Bose Particles or Bosons**. They have integral spins $0, \hbar, 2\hbar, 3\hbar, \dots$

S.N. Bose and Einstein established an appropriate statistics for such particles which is called **Bose – Einstein statistics**. In this statistics, it is specially postulated that all the quantum states appear with equal probability and each quantum state can have one or more particles in it. α - particles, photons, phonons etc., are examples of bosons.

- (ii) The particles whose spin angular momentum is half odd integral multiples of \hbar are called **Fermi particles or Fermions**. They have spins $\frac{1}{2} \hbar, \frac{3}{2} \hbar, \frac{5}{2} \hbar, \dots$ Fermi and Dirac established appropriate statistics for these particles which is called **Fermi – Dirac statistics**.

These particles obey the **Pauli Exclusion Principle** which states that there can be only one fermions and not more in one quantum state. Electrons, protons, neutrons are examples of fermions.

5.10 Bose - Einstein statistics:

Derivation of Bose – Einstein Distribution Law:

Consider an assembly of N bosons. They are identical and indistinguishable. No restriction is imposed as to the number of particles that may occupy a given cell. Let us now consider a box divided into g_i sections by $(g_i - 1)$ partitions and n_i indistinguishable particles to be distributed among these sections. The permutations of n_i particles and $(g_i - 1)$ partitions simultaneously is given by $(n_i + g_i - 1)!$. But this includes also the permutations of n_i particles among themselves and also $(g_i - 1)$ partitions among themselves, as both these groups are internally indistinguishable.

Hence the actual number of ways in which n_i particles are to be distributed in g_i sub levels is

$$\frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!}$$

Therefore, the total number of the distinguishable and distinct ways of arranging N particles in all the available energy states is given by

$$W = \prod \frac{(n_i + g_i - 1)!}{n_i! (g_i - 1)!} \dots\dots\dots(1)$$

n_i and g_i are large numbers. Hence we may neglect 1 in the above expression.

$$W = \prod \frac{(n_i + g_i)!}{n_i! g_i!} \dots\dots\dots(2)$$

$$\ln W = \sum [\ln(n_i + g_i)! - \ln n_i! - \ln g_i!] \dots\dots(3)$$

As n_i and g_i are large numbers, we can use Stirling approximation.

$$\ln W = \sum (n_i + g_i) \ln(n_i + g_i) - n_i \ln n_i - g_i \ln g_i \dots\dots (3)$$

Here, g_i is not subject to variation and n_i varies continuously.

For most probable distribution, $\delta \ln W_{max} = 0$

Hence, if the W of Eq.(3) represents a maximum,

$$\delta \ln W_{max} = \sum [\ln(n_i + g_i) - \ln n_i] \delta n_i = 0 \dots\dots\dots(4)$$

The total number of particles and total energy are constants.

$$\sum \delta n_i = 0 \dots\dots\dots(5)$$

$$\sum E_i \delta n_i = 0 \quad \dots\dots\dots(6)$$

Multiply Eq. (5) by $-\alpha$, and Eq (6) by $-\beta$ and adding to Eq. 4, we get

$$\sum [\ln(n_i + g_i) - \ln n_i - \alpha - \beta E_i] \delta n_i = 0$$

The variations δn_i are independent of each other, Hence we get

$$\ln \left(\frac{n_i + g_i}{n_i} \right) - \alpha - \beta E_i = 0$$

$$n_i = \frac{g_i}{(e^{\alpha + \beta E_i}) - 1} \quad \dots\dots\dots(7)$$

$$n_i = \frac{g_i}{(e^{\alpha} e^{E_i/kT}) - 1} \quad \dots\dots\dots(8)$$

This is known as Bose – Einstein distribution law.

Let us define a quantity $f_{BE}(E_i) = \frac{n_i}{g_i}$

$f(E_i)$ is called the ‘occupation index’ of a state of energy E_i .

$$f_{BE}(E_i) = \frac{1}{(e^{\alpha} e^{E_i/kT}) - 1}$$

$f(E)$ is called the *occupation probability or the distribution function*.

Properties of Photon gas:

- (i) Photons are particles of zero rest mass
- (ii) Photons are bosons (i.e., the particles with spin 1) and have two modes of propagation (due to a clockwise and a counter clockwise polarization)
- (iii) Photons are mutually indistinguishable
- (iv) The number of photons is not conserved because at the instant of emission a new quantum is formed. If photon of frequency ν is absorbed by the walls of the enclosure, several photons may be emitted provided the total energy of the system is conserved.

5.11 Fermi – Dirac statistics:

5.11.1 Derivation of Fermi – Dirac Distribution Law

F.D. statistics is obeyed by indistinguishable particles of half – integral spin that have antisymmetric wave functions and obey Pauli exclusion principle. Consider fermions with the total energy E . Suppose that n_1 particles occupy the first energy level with energy E_1 , n_2 particles occupy the second energy level with energy E_2 and so on. Let us now find out the total number of ways in which n_i particles can be distributed in g_i cells having the same energy E_i .

The number of distinguishable arrangements of n_i particles in g_i cells is

$$\frac{g_i!}{n_i!(g_i - n_i)!}$$

The total number of Eigen states for the whole system is given by

$$W = \prod \frac{g_i!}{n_i!(g_i - n_i)!} \dots\dots\dots(1)$$

Taking the natural logarithm on both sides,

$$\ln W = \sum [\ln g_i! - \ln n_i! - \ln (g_i - n_i)!]$$

Applying Stirling's approximation

$$\ln W = \sum [g_i \ln g_i - g_i - n_i \ln n_i + n_i - (g_i - n_i) \ln (g_i - n_i) + (g_i - n_i)]$$

$$\ln W = \sum [g_i \ln g_i - n_i \ln n_i - (g_i - n_i) \ln (g_i - n_i)] \dots\dots\dots(2)$$

Here g_i is not subject to variation and n_i varies continuously.

For the most probable distribution, $\delta \ln W_{max} = 0$

$$\delta \ln W_{max} = \sum [-\ln n_i + \ln (g_i - n_i) \delta n_i] = 0 \dots\dots\dots(3)$$

$$\sum \delta n_i = 0 \dots\dots\dots(4)$$

$$\sum E_i \delta n_i = 0 \dots\dots\dots(5)$$

Multiply Eq. (4) by $-\alpha$, and Eq (5) by $-\beta$ and adding to Eq. 3, we get

$$\sum [-\ln n_i + \ln(g_i - n_i) - \alpha - \beta E_i] \delta n_i = 0$$

As the variations δn_i are independent of each other, we get

$$\ln \left(\frac{g_i - n_i}{n_i} \right) - \alpha - \beta E_i = 0$$

$$n_i = \frac{g_i}{(e^{\alpha} e^{\beta E_i}) + 1} \quad \dots\dots\dots(6)$$

This is known as Fermi – Dirac Distribution law.

$\beta = 1/kT$ and $\alpha = - E_f/kT$ where E_f is called Fermi energy

$$E_f = -\alpha kT \quad \dots\dots\dots(7)$$

Definition of Fermi energy

At the absolute zero of temperature the maximum kinetic energy that a free electron can have is called the Fermi energy E_f .

$$n_i = \frac{g_i}{[e^{\left(\frac{E_i - E_f}{kT}\right)} + 1]}$$

The F.D distribution function is

$$f_{FD}(E_i) = \frac{1}{(e^{\alpha} e^{E/kT}) + 1}$$

5.11.2 Applications of Fermi - Dirac Statistics:

Electron gas (Theory of Fermi Gas and Fermi Energy)

Various properties of the metals such as electrical and thermal conductivities can be explained on the assumption that the electrons in the metal are free to move exactly like the particles of a gas. Metals have free electrons which are free to move inside metal surface but are not free to come out and leave the surface due to surface barrier (Coulomb potential well). Electrons are fermions. Thus such a system with a large number of electrons moving freely inside is an example of **Fermi gas**. We can study the behaviour of the electrons moving freely inside, is an example of F –D statistics by considering them to form an electron gas in the metal.

Expression for Fermi energy

The “free electron gas” in a solid obeys Fermi – Dirac statistics. Suppose in an assemblage of fermions, there are $M(E)$ allowed quantum states in an energy range between E and $E + dE$ and $N(E)$ is the number of particles in the same range. Then $N(E)$ quantum states are filled and $M(E) - N(E)$ are vacant.

The F –D distribution function $f(E)$ is defined as:

$$f(E) = \frac{N(E)}{M(E)} = \frac{1}{1 + e^{(E - E_f)/kT}} \dots\dots\dots(1)$$

$\frac{N(E)}{M(E)}$ represents the fraction of the possible quantum states which is occupied. The distribution of electrons among the levels is usually described by the distribution function $f(E)$. It is defined as the probability that the level E is occupied by an electron. Thus, if the level $f(E) = 1$. In general $f(E)$ has a valued between zero and unity.

The distribution function for electrons at $T = 0K$ has the form $f(E) = 1$ when $E < E_f$

And $f(E) = 0$ when $E > E_f$ (2)

That is, all levels below E_f are completely empty. As the temperature rises, $f(E)$ changes from 1 to 0 more and more gradually.

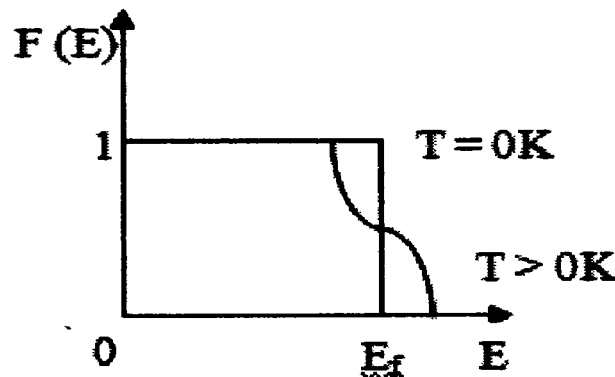


Fig 5.7

For $E = E_f$, $f(E) = \frac{1}{1 + e^0} = \frac{1}{2}$, at all temperatures.

Thus, the probability of finding an electron with energy equal to the Fermi – energy in a metal is $\frac{1}{2}$ at any temperature.

Since the electrons are confined inside the crystal, their wave properties will limit the energy values which they may have. Let $g(E) dE$ be the number of quantum

states available to electron with energies between E and $E + dE$. It can be shown that

$$g(E)dE = \frac{8\sqrt{2}\pi V m^{1/2}}{h^3} \sqrt{E} dE \quad \dots\dots\dots(3)$$

Here, m is the mass of the electrons and V is the volume of the electron gas.

We can calculate the Fermi - Energy E_f by filling up the energy states in the metal sample with the N free electrons it contains in order of increasing energy, starting from $E = 0$. The highest state to be filled will then have the energy $E = E_f$ by definition. The number of electrons that can have the same energy E is equal to the number of states that have this energy, since each state is limited to one electron. Hence,

$$\begin{aligned} N &= \int_0^{E_f} g(E)dE = \frac{8\sqrt{2}\pi V m^{1/2}}{h^3} \int_0^{E_f} \sqrt{E} dE \\ &= \frac{16\sqrt{2}\pi V m^{3/2}}{3h^3} E_f^{3/2} \\ E_f &= \left(\frac{h^2}{2m}\right) \left(\frac{3N}{8\pi V}\right)^{2/3} \quad \dots\dots\dots(4) \end{aligned}$$

The quantity N/V is the density of free electrons. N/V represents the number of free electrons per unit volume of the metal.

As effective temperature of the electron gas, known as the Fermi - temperature , is defined by

$$T_f = E_f / k$$

Definition of Fermi Energy: At the absolute zero of temperature the maximum kinetic energy that a free electron can have is called the Fermi Energy, E_f .

5.12 Summary:

- Probability of an event = $\frac{\text{Number of cases in which the event occurs}}{\text{total number of cases}}$
- *This principle of assuming equal probability for events which are equally likely to occur is known as the principle of equal a priori probability.*
- *The thermodynamic probability of a particular macrostate is defined as the number of microstates corresponding to that macrostate.*
- Nernst heat theorem.

$$S = k \log W + C,$$

- Additive law of probability.

$$P = p_1 + p_2 + p_3 + \dots + p_N = \sum_{i=1}^N p_i$$

- **Multiplication Rule: Probability**

$$P = p_1 \times p_2$$

- The total energy of the system is

$$E = n_1 E_1 + n_2 E_2 + \dots = \sum_i n_i E_i$$

- Maxwell – Boltzmann distribution law.

$$n_i = g_i e^{-\alpha} e^{-\beta E_i}$$

M – B Distribution in terms of temperature

$$n_i = g_i e^{-\alpha} e^{-E_i/kT}$$

- **M – B Distribution in terms of temperature**

$$n_i = g_i e^{-\alpha} e^{-E_i/kT}$$

- **Maxwell – Boltzmann velocity distribution law**

$$n(v)dv = \frac{\sqrt{2} \pi N m^{1/2}}{(\pi kT)^{1/2}} v^2 e^{-mv^2/2kT} dv$$

- Identical particles in a system are regarded as those particles which when interchanged in the system will not make any change in it.
- The particles whose spin angular momentum are intergral multiples of \hbar are called the **Bose Particles or Bosons**.
- The particles whose spin angular momentum are half odd integral multiples of \hbar are called **Fermi particles or Fermions**
- Bose – Einstein distribution law.

$$n_i = \frac{g_i}{(e^{\alpha} e^{E_i/kT}) - 1}$$

- Fermi – Dirac Distribution law.

$$n_i = \frac{g_i}{(e^{\alpha} e^{\beta E_i}) + 1}$$

- **Definition of Fermi energy** :At the absolute zero of temperature the maximum kinetic energy that a free electron can have is called the Fermi energy E_f .

$$E_f = \left(\frac{\hbar^2}{2m}\right) \left(\frac{3N}{8\pi V}\right)^{2/3}$$

Check your progress:

1. Calculate the volume of six dimensional phase space of a state. What is its unit?

Ans:-----

Check your progress:

2. An electron gas obeys the Maxwell – Boltzmann statistics. Calculate the average thermal energy (in e V) of an electron in the system at 300 K.

Ans:-----

Check your progress:

3. Explain the law of equipartition of energy

Ans:-----

Check your progress:

4. What is electron gas?

Ans:-----

Check your progress:

5. Explain Zero Probability.

Ans:-----

Check your progress:

6. Calculate the volume of six dimensional phase space of a state. What is its unit?

Ans:-----

Check your progress:

7. We throw a die twice and obtain two numbers. What is the probability that these numbers are 6 and 4 precisely in that order?

Ans:-----

Check your progress:

8. Compare the three statistics (M.B , B.E, F.D)

Ans:-----

5.13. Unit – end Exercises:

1. What are ensembles?
2. What is phase space?
3. Explain microstates and macro states.
4. What is Thermodynamic probability?
5. Explain Boltzmann theorem on entropy and probability.

6. State the fundamental postulates of statistical mechanics.
7. Derive the Boltzmann relation between entropy and probability.
8. Derive the Maxwell – Boltzmann distribution law.
9. Obtain an expression for Bose Einstein distribution law. Explain photon gas.
10. (a) Derive the Fermi Dirac Statistical distribution law.
(b) Compare the three statistics.

5.14 Problems for discussion:

1. A card is drawn from a well shuffled pack of 52 cards. Calculate the probability for this card to be either a king or a queen.
2. Calculate the kinetic energy of one gram mole of oxygen at 300 K. [R=8.31 J/mole – K]
3. Calculate the Fermi energy at absolute zero for copper assuming that it has one free electron per atom. Density of copper = 9000 kgm/m³. Atomic weight = 63.5
4. A gas has only two particles a and b. Show with the help of diagrams how these two particles can be arranged in three quantum series 1,2,3 using (i) Maxwell – Boltzmann (ii) Bose – Einstein and (iii) Fermi – Dirac statistics.
5. Find the Fermi energy of copper on the assumption that each copper atom contributes one free electron to the electron gas. The density of copper is 8.94 x 10³ kg/m³
6. Suppose there are just three cells in phase space labelled 1,2,3, and two particles. A and B. Enumerate the different macrostates and the microstates corresponding to each of them.

5.15. Answer for Check your progress & Problems for discussion:

Answers for Check your progress:

- 1) According to Heisenberg's uncertainty principle, the position and momentum of a particle cannot be determined simultaneously to any desired degree of accuracy.

If Δx denotes the error in determining its position and Δp the error in determining its momentum, then according to this principle,

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

The product of the two errors is thus approximately of the order of Planck's constant h ,

i.e., $\Delta x \cdot \Delta p \approx h$.

Let Δx = Uncertainty in measuring the x coordinate of the particle.

Δp_x = Uncertainty in measuring the x component of the momentum of the particle.

Then, $\Delta x \times \Delta p_x = h$

$$\Delta y \Delta p_y = h$$

$$\Delta z \Delta p_z = h$$

Volume of phase space cell

$$H = (\Delta x)(\Delta p_x)(\Delta y)(\Delta p_y)(\Delta z)(\Delta p_z) = h^3$$

The unit of phase – space volume = $(J - S)^3$

2) Answer:

$$\begin{aligned} E &= \frac{3}{2} kT = \frac{3}{2} \times (1.38 \times 10^{-23}) \times 300 \text{ J} \\ &= \frac{3 \times (1.38 \times 10^{-23}) \times 300}{2 \times (1.6 \times 10^{-19})} \text{ eV} = 0.039 \text{ eV} \end{aligned}$$

3) Answer:

Law of Equipartition of Energy Statement:

The total kinetic energy of a dynamical system consisting of a large number of particles in thermal equilibrium is equally divided among its all degrees of freedom and the average energy associated with each degree of freedom is $(1/2) kT$.

Here, k is Boltzmann's constant and T is the absolute temperature of the system.

This principle is true for all degrees of freedom – translational, rotational or vibrational.

4) Answer: The valence electrons in a metal are free to roam in the ionic array of positive fixed nuclei. These mobile electrons in a metal behave, more or less as particles of a perfect gas and form what is known as electron gas (or Fermi-gas). These electrons, however, cannot come out of the metal surface because of surface potential barrier (work function).

5) Answer: If we want to know the probability of the die coming up with a face marked with a number 7. The die has only six faces marked serially from 1 to 6. There is no face marked as 7. Therefore, probability of appearing a number 7 is zero i.e.,

$$P(\text{number } 7) = \frac{0}{6} = 0$$

6) **Answer:** The probability that the first throw gives a 6 is $\frac{1}{6}$. Similarly, the probability that the second throw gives a 4 is also $\frac{1}{6}$. These two events are independent.

$$\text{Required probability} = \frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$$

7) **Answer:**

Bose – Einstein	Fermi - Dirac
<ol style="list-style-type: none"> 1. Particles are indistinguishable and quantum states are taken into consideration. 2. No restriction on the number of particles in a given quantum state. 3. Applicable to photons and symmetrical particles 4. Volume in phase space is known, (h^3). 5. The energy at absolute zero is taken to be zero 6. At high temperatures, Bose-Einstein distribution approaches Maxwell's distribution. 7. The most probable distribution is given by $\frac{n_i}{g_i} = \frac{1}{[e^{\alpha + \beta \epsilon_i} + 1]}$ 	<ol style="list-style-type: none"> 1. Particles are indistinguishable and quantum states are taken into consideration. 2. Only one particle may be in a given quantum state. 3. Applicable to electrons and elementary particles 4. Volume in phase space is known, (h^3). 5. Even at absolute zero, the energy is not zero. 6. At high temperatures, Fermi distribution approaches Maxwell- Boltzmann distribution. 7. The most probable distribution is given by $\frac{n_i}{g_i} = \frac{1}{[e^{\alpha + \beta \epsilon_i} - 1]}$

Answers for Problems for discussions:

1) Solution:

We are taking out one card out of 52 cards of pack. So the total number of ways in which the event can occur is $N = 52$.

But we want to draw a specific card i.e. king. There are 4 kings in a pack of cards. Therefore, the number of ways favourable to the first event, $m_1 = 4$

Probability of drawing a king , $P_1 = \frac{m_1}{N} = \frac{4}{52} = \frac{1}{13}$

The number of ways in which second event i .e. drawing a queen may happen, $m_2 = 4$, as there are four queens too.

Probability of drawing a king , $P_2 = \frac{m_2}{N} = \frac{4}{52} = \frac{1}{13}$

Both the events are mutually exclusive. Therefore the probability that the card drawn is either a king or a queen is

$$P = P_1 + P_2 = \frac{1}{13} + \frac{1}{13} = \frac{2}{13}$$

2) **Solution:** Oxygen is a diatomic molecule. It has three degrees of freedom of translational motion and two degrees of freedom of rotational motion. i.e, in all five degrees of freedom.

Here, $T = 300 \text{ K}$, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$

Total K.E. per mole = $\frac{5}{2} RT = \frac{5}{2} \times 8.31 \times 300 = 6232 \text{ J}$

3) **Solution:**

$$\begin{aligned} E_f &= \left(\frac{h^2}{2m} \right) \left(\frac{3N}{8\pi V} \right)^{2/3} \\ &= \frac{(6.63 \times 10^{-34})^2}{2 \times (9.11 \times 10^{-32})} \left[\frac{3}{8\pi} \left\{ \frac{6.02 \times 10^{26}}{\frac{635}{9000}} \right\} \right]^{2/3} \\ &= 1.128 \times 10^{-18} \text{ J} \\ &= \frac{1.128 \times 10^{-18}}{1.6 \times 10^{-19}} \text{ eV} \\ &= 7.05 \text{ eV.} \end{aligned}$$

4) **Solution: (i) Maxwell – Boltzmann Statistics**

The two particles are distinguishable

There is no limit to the number of particles in any one state.

The total number of way is $3^2 = 9$.

States	Possible Distribution in various Status							
1	a	b	-	a	b	ab	-	-
2	b	a	a	-	-	-	ab	-
3	-	-	b	b	a	-	-	ab

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(ii) Bose – Einstein Statistics:

If a and b are quantum particles, they are indistinguishable. Thus they have to be given the same name, say, α

There is no limit to the number of particles in any one state

The total number of ways = 6

States	Possible Distribution in various Status					
1	a	a	-	aa	-	-
2	a	-	a	-	aa	-
3	-	a	a	-	-	aa

(iii) Fermi – Dirac Statistics:

The particles are indistinguishable are not more than one particle can be in any one state.

The total number of ways = 3

States	Possible Distribution in various Status		
1	a	a	-
2	a	-	a
3	-	a	a

5) **Solution:** The Fermi energy E_F is given by

$$E_r = \left(\frac{h^2}{2m} \right) \left(\frac{3N}{8\pi V} \right)^{2/3}$$

Here, m = mass of the electron = 9.11×10^{-31} kg.

$\frac{N}{V}$ = number of free electrons per unit volume of the metal. Let the atomic weight of the metal be M and let its density be ρ

Volume of one kilo mole of the metal = $V = \frac{M}{\rho} m^3$

No. of atoms per kilo mole = N = Avogadro's number.

Each atom contributes one free electron.

No. of free electrons per unit volume is

$$\frac{N}{V} = \frac{N}{M/\rho} = \frac{6.02 \times 10^{26}}{(63.54)/(8.94 \times 10^3)} = 8.48 \times 10^{28} \text{ electrons/m}^3$$

$$\frac{(6.63 \times 10^{-34})^2}{2 \times (9.11 \times 10^{-31})} \left(\frac{3}{8\pi} \times 8.48 \times 10^{28} \right)^{2/3} = 1.13 \times 10^{-18} \text{ J}$$

$$= 7.04 \text{ eV.}$$

6) **Solution:** The possible macrostates are

	(i)	(ii)	(iii)	(iv)	(v)	(vi)
n_1	2	0	0	0	1	1
n_2	0	2	0	1	0	1
n_3	0	0	2	1	1	0

For macrostate

(i), there is only one possible microstate, viz., AB
 Similar remarks apply to (ii) and (iii). Corresponding to (iv), we have the microstates.

 A B

and

 B A

1 2 3

1 2 3

Similarly, two microstates correspond to each of (v) and (vi).

5.16. Suggested Readings:

6. Thermal physics- R.Murugesan , S.Chand S.Chand & Co, New Delhi..
7. Heat and Thermodynamics -J.B.Rajram and C.L.Arora, S.Chand & Co, New Delhi,2004.
8. Fundamental of Statical Mechanics - A.K.Dasgupta ,NCBA (p) Ltd , Calcutta.

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