93. Calculate the change in entropy when 20 grams of ice at 0°C is converted into water at the same temperature.
[**Ans.** 586 cal/K]

94. Calculate the change in entropy when 10 kg. of water at 100°C is converted into steam at the same temperature.
[**Ans.** 14480 cal/K]

95. Calculate the increase in entropy when 5 g of ice at −10°C is converted into steam at 100°C. Sp. heat of ice = 0·5 ; Latent heat of ice = 80 cal/g ; Latent heat of steam = 540 cal/g.
[**Ans.** 10·35325 cal/K]

96. Two gram molecules of a gas expands isothermally to four times its initial volume. Calculate the change in its entropy in terms of the gas constant.
[**Ans.** $2{\cdot}774\ \frac{R}{J}$ cal/K]

97. 100 g of water at 0°C is mixed with an equal mass of water at 80°C. Calculate the resultant increase in entropy.
[**Ans.** 1·612 cal/K]

98. Calculate the change in entropy when 100 g of water at 15°C is mixed with 160 g of water at 40°C. Specific heat of water may be assumed as equal to 1. [**Ans.** −0·130 cal/K]

99. Calculate the change in the melting point of wax for a pressure of 50 atmospheres from the following data. Melting point of wax = 64°C. Specific volume of solid at 64°C = 1·161 and that of the liquid at 64°C = 1·166. Latent heat = 97 cal/g.
[**Ans.** +0·1702 K or +0·1702°C]

100. Calculate the change in temperature of the boiling point of water due to a change of pressure of 1 cm of Hg. L = 536 cal/g. Volume of 1 g of water at 100°C = 1 cc and volume of 1 g of saturated steam at 100°C = 1600 cc. [*Agra 1962*]
[**Ans.** +0·3531 K or +0·3531°C]

101. Calculate the pressure required to make ice freeze at −1°C. Change in specific volume when one gram of water freezes into ice is equal to 0·091 cm^3. $J = 4{\cdot}2 \times 10^7$ ergs/cal. One atmosphere = 10^6 dynes/cm^2. Latent heat of ice = 80 cal/g.
(*Agra 1963*)
[**Ans.** 136·2 atmospheres]

102. Calculate the change in entropy when one gram of ice is mixed with 2 millilitres of water at 55°C. Assume that the specific heat and the specific gravity of water remain constant (*i.e.* equal to 1 in both the cases) between 0°C and 55°C. Latent heat of ice=80 cal/g. [*Agra 1964*]
[**Ans.** +0·03372 cal/K]

103. A Carnot's engine takes in 1000 kilocalories of heat from a reservoir at 627°C and exhausts it to a sink at 27°C. (*a*) What is its efficiency ? (*b*) How much work does it perform ? Express it (*i*) in ergs (*ii*) kilo-Watt hours (*iii*) electron volts. (*Agra 1965*)
[**Ans.** (*a*) 66·67% (*b*) (*i*) 14×10^{12} ergs.
(*ii*) 0·39 kilo-Watt hours (*iii*) $8{\cdot}75 \times 10^{24}$ eV]

7

Liquefaction of Gases

7·1 Introduction

For a long time it was thought that air remains in the gaseous state at all temperatures. Gases like oxygen, nitrogen, hydrogen, helium etc., were termed as permanent gases. Freezing mixture could liquefy chlorine, hydrogen sulphide, sulphur dioxide, ammonia, hydrochloric acid etc. under high pressure. Andrew's experiments on CO_2 in 1862 showed that below the critical temperature, a gas can be liquefied by mere application of pressure but it cannot be liquefied above the critical temperature, however large the applied pressure may be. Below the critical temperature, the gas is termed as vapour and above the critical temperature it is called a gas.

In 1877, Pictet liquefied oxygen by Cascade process. Linde was able to liquefy air in 1896 by Joule-Kelvin effect. Using the principle of Joule-Kelvin effect, hydrogen and helium were also liquefied.

	Critical Temp.	*Boiling Point*
CO_2	−31·1°C	−78·6°C
Oxygen	−118·8°C	−183°C
Nitrogen	−146°C	−195·8°C
Hydrogen	−240°C	−252·8°C
Helium	−267·8°C	−269·8°C

7·2 Cascade Process—Liquefaction of Oxygen

In 1878 Pictet was able to liquefy oxygen. Later on K. Onnes modified the apparatus as shown in Fig. 7·1.

The apparatus consists of compression pumps P_1, P_2, and P_3. A, B and C are the outer jackets containing cold water, liquid methyl chloride and liquid ethylene. The pump P_1 compresses methyl chloride gas and it is cooled by cold water circulating in the jacket A. As the critical temperature of methyl chloride is 143°C, it is liquefied. Liquid methyl chloride circulates in the outer jacket B.

The pump P_2 compresses ethylene gas and it is surrounded by the outer jacket B containing liquid methyl chloride at about —24°C.

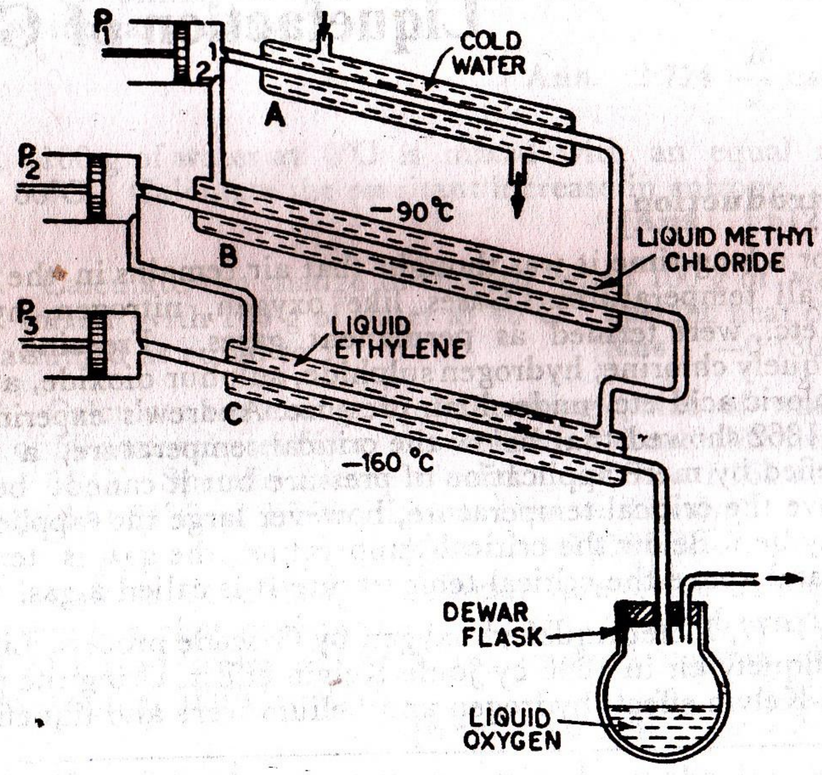


Fig. 7·1

Liquid methyl chloride is allowed to boil under reduced pressure with the help of the pump P_1. The temperature of B reaches —90°C. The critical temperature of ethylene is 10°C. It is cooled to —90°C and due to compression it gets liquefied.

The liquid ethylene in the jacket C is allowed to boil under reduced pressure with the help of the pump P_3 and finally a temperature of —160°C is reached. The critical temperature for oxygen is —118·8°C. Oxygen is compressed to a pressure of about 25 atmospheres and is passed through a spiral tube surrounded by the jacket C. Oxygen gets liquefied and is collected in a Dewar flask. Oxygen in the form of gas in the Dewar flask is circulated back to the pump P_3 and the process is repeated.

Liquefaction of Nitrogen. Liquid oxygen has a normal boiling point —183°C. It is allowed to boil under reduced pressure and a temperature of —218°C is reached. The critical temperature of nitrogen is —146°C. By adding a fourth unit containing liquid oxygen, nitrogen can be liquefied. Cascade process cannot be used to

liquefy hydrogen (T_c = —240°C), neon (T_c = —229°C) and helium (T_c = —268°C); because in this process the lowest temperature obtainable is —240°C.

7·3 Liquefaction of Air—Linde's Process

In this process, Joule-Kelvin effect is applied. Linde was able to liquefy air in 1896 using this effect. The apparatus used is shown in Fig. 7·2.

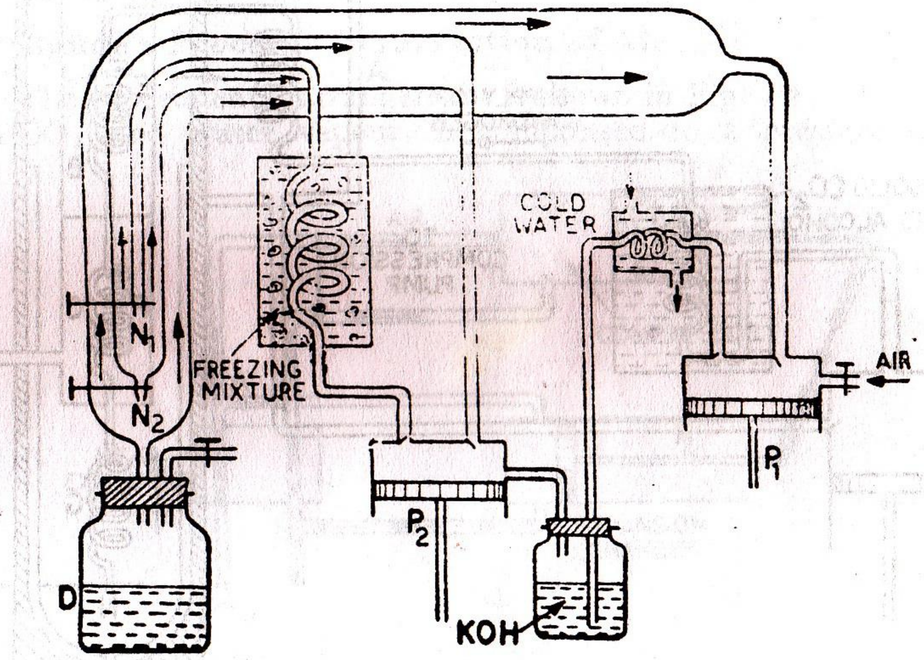


Fig. 7·2.

The pump P_1 compresses air to a pressure of about 25 atmospheres and is passed through a tube surrounded by a jacket through which cold water is circulated. This compressed air is passed through KOH solution to remove CO_2 and water vapour.

This air, free from CO_2 and water vapour, is compressed to a pressure of 200 atmospheres by the pump P_2. This air passes through a spiral tube surrounded by a jacket containing a freezing mixture. This cooled air at high pressure and at a temperature of —20°C is allowed to come out of the nozzle, N_1. Joule-Kelvin effect takes place and the incoming air is cooled. The cooled air is circulated back to the pump P_2 and is compressed. It passes through the nozzle N_1 and is further cooled. This cooled air is allowed to pass through the nozzle N_2 (from high pressure to low pressure side) and is further cooled. As the process continues, after a few cycles, air gets cooled to a sufficiently low temperature and after coming out of the nozzle N_2 gets liquefied and is collected in the Dewar flask. The unliquefied air is again circulated back to the pump P_1 and the process is repeated.

The whole of the apparatus is packed in cotton wool to avoid any conduction or radiation.

7·4 Liquefaction of Hydrogen

Hydrogen cannot be liquefied by Cascade process because its critical temperature is —240°C. Linde's ordinary apparatus used for the liquefaction of air cannot be used for hydrogen because the temperature of inversion for hydrogen is —83°C. The gas must initially be cooled to a temperature lower than the temperature of inversion for the cooling to take place due to Joule-Kelvin effect. The original apparatus designed by Dewar (1898) was improved

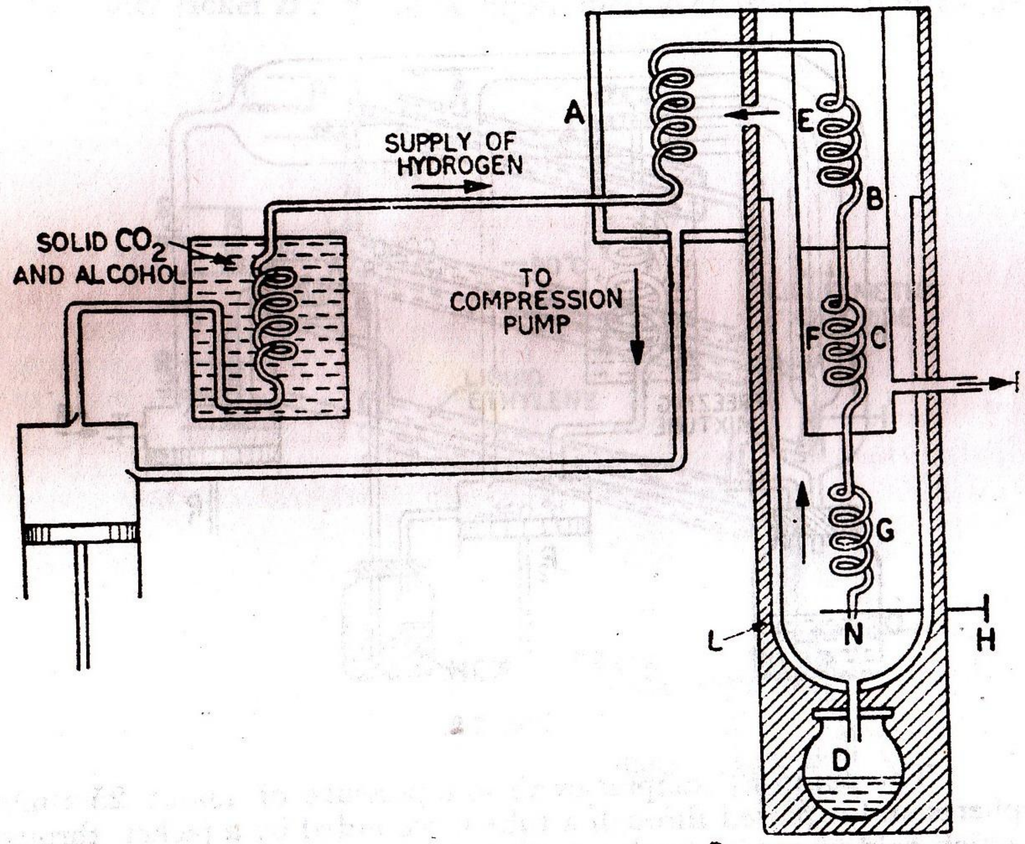


Fig. 7·3.

later by Travers, Olszewski, Nernst and others (Fig. 7·3). To have complete insulation the whole apparatus is enclosed in an outer Dewar flask *L*.

Hydrogen under a pressure of 200 atmospheres is passed through a coil immersed in solid CO_2 and alcohol. It enters the coil in the chamber *A* where it is further cooled by the outgoing hydrogen. The chamber *B* contains liquid air and cools hydrogen in the coil *E*. In the chamber *C* liquid air is allowed to boil under reduced pressure (10 cm of Hg) and hydrogen in the coil *F* is cooled to a temperature of —200°C. This cooled hydrogen passes through the regenerative coil *G* and the nozzle *N*. Hydrogen is cooled further due to Joule-Kelvin effect. The cooled hydrogen coming from the nozzle *N* is allowed to circulate back to the pump as shown in Fig. 7·3. The process of regenerative cooling continues and after some time hydrogen gets liquefied and is collected in the Dewar flask *D*.

7·5 Solidification of Hydrogen

By boiling liquid hydrogen under reduced pressure (10 mm of Hg) Dewar was able to solidify hydrogen. Liquid hydrogen was contained in a double walled thermos tube which was immersed in an outer bath containing liquid hydrogen. The pressure inside the tube was reduced and the temperature of hydrogen in the tube decreased below —259°C. Liquid hydrogen did not solidify but was only super-cooled below the freezing point. By allowing a little trace of air to leak into the apparatus it was possible to obtain solid hydrogen. Solid hydrogen is white in colour.

7·6 Claude's Process—Liquefaction of Air

The experimental arrangement is shown in Fig. 7·4. Air, free from CO_2 and water vapour, is compressed to a pressure of 40

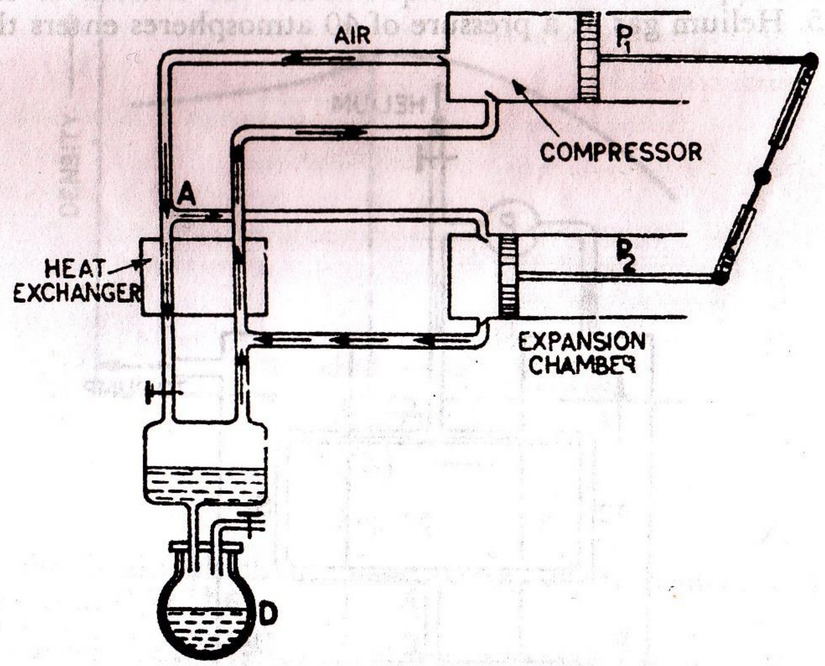


Fig. 7·4

atmospheres by the compressor P_1. Initially air is cooled by passing it through a coil immersed in a freezing mixture. At the point A, 80% of the compressed air goes to the expansion chamber and 20% to the heat exchanger. In the expansion chamber air expands, does external work and drives the piston P_2 outwards. Due to adiabatic expansion, air gets cooled. The expansion chamber and the compressor are coupled so that when P_2 moves outwards, P_1 moves inwards and compresses the air in the compressor.

The cooled air from the expansion chamber passes through the heat exchanger and takes heat from it. 20% of air, passing through the tube in the heat exchanger, gives heat and consequently gets cooled. This regenerative cooling process continues and when the temperature of air reaches the liquefaction temperature, it gets liquefied and is collected in the Dewar flask *D*.

The main problem in this process is that of solidification of lubricants at low temperatures. Petroleum ether is found to be a useful lubricant at low temperatures. Once air gets liquefied, it itself serves as a lubricant.

This process is complicated apart from the problem of lubricants. Linde process is commercially used for the liquefaction of air.

7·7. Liquefaction of Helium—K. Onnes Method

K. Onnes liquefied helium in 1908. The temperature of inversion of helium is —240°C. Kapitza has liquefied helium by precooling it and passing it through a coil surrounded by a bath containing liquid hydrogen boiling under reduced pressure. In this way helium was cooled to —258°C.

The apparatus used for liquefaction of helium is shown in Fig. 7·5. Helium gas at a pressure of 40 atmospheres enters the spiral

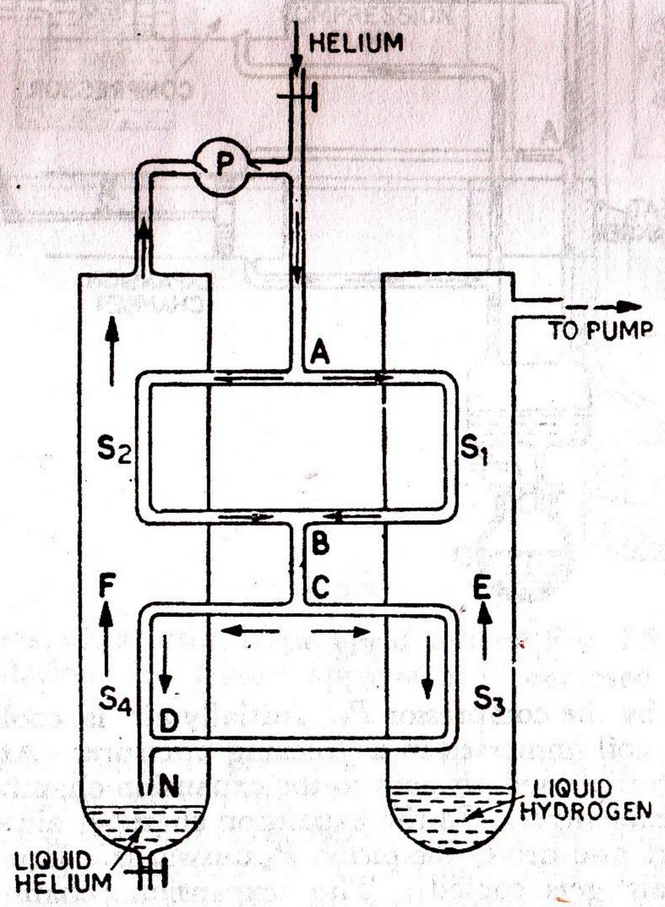


Fig. 7·5

tube at *A*. It is divided into two portions. Helium passing through the spiral in *E* is cooled because it is surrounded by hydrogen boiling under reduced pressure. The other portion of helium gas passing through the spiral in *F* is cooled due to outgoing cooled helium gas. Similar processes take place in the spirals S_3 and S_4. The process is repeated and when the temperature of helium is sufficiently low, it gets liquefied after passing through the nozzle *N*. At *N* cooling takes place due to Joule-Kelvin effect. This outgoing helium is compressed

again by *P* and fed back to the spirals S_1 and S_2. Liquefied helium is collected in the Dewar flask. The whole apparatus is surrounded by Dewar flasks to provide perfect heat insulation.

Simon has been able to liquefy helium by using activated charcoal. When helium is adsorbed by charcoal, heat is evolved and when it is desorbed (removed), the temperature of the gas falls. Helium is adsorbed in large quantities by activated charcoal immersed in liquid hydrogen. The apparatus is enclosed in an evacuating vessel to minimize heat exchanges with the surroundings. On pumping off helium, its temperature falls considerably and it gets liquefied.

7·8 Helium I and Helium II

K. Onnes observed no sign of solidification when liquid helium was cooled at ordinary pressures. It was found that at a temperature

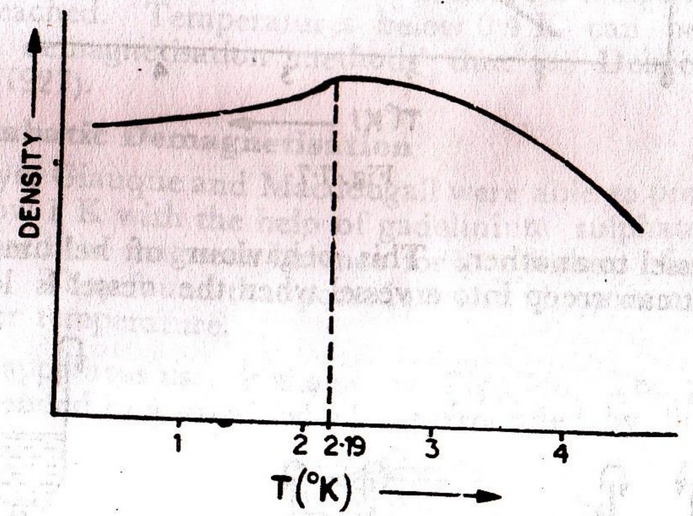


Fig. 7·6

of 2·19 K, the liquid which was contracting when cooled, suddenly began to expand (Fig. 7·6).

The specific heat of liquid helium increases up to 2·19 K and at this temperature there is a sudden and abnormal increase in the specific heat. Beyond 2·19 K, the specific heat first decreases and then increases (Fig. 7·7).

The specific heat—temperature graph resembles λ and hence this temperature at which the specific heat changes abruptly (2·19 K) is called the λ-point. Liquid helium above 2·19 K is called helium I because it behaves in a normal way and below 2·19 K it is called helium II because of its abnormal properties.

Viscosity of liquid helium I decreases with decrease in temperature and this property is contrary to the property of a liquid but it resembles that of a gas. The viscosity of helium II is practically zero and it can flow rapidly through narrow capillary tubes.

The thermal conductivity of helium II has an abnormally high value and it is many times more than that of copper and silver.

Helium II forms a thin film on all solid surfaces This film is called the *Rolling film.* It is through this film that helium II flows

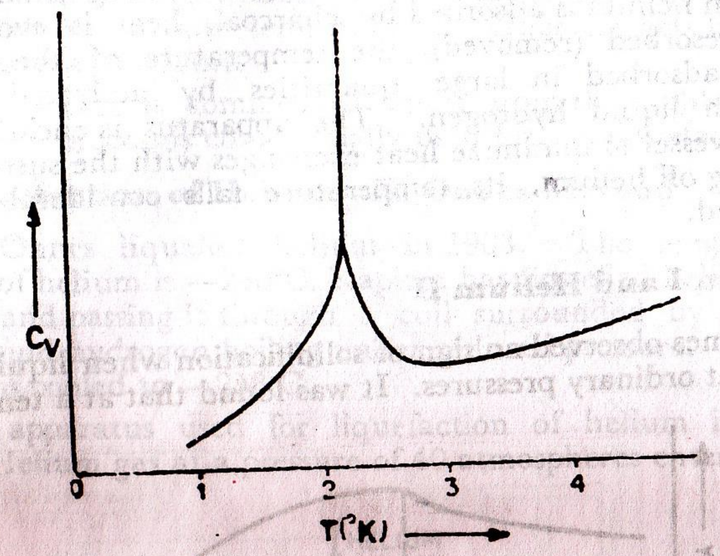


Fig. 7·7

from one vessel to another. This behaviour of helium II is very peculiar. It can creep into a vessel when the vessel is lowered into

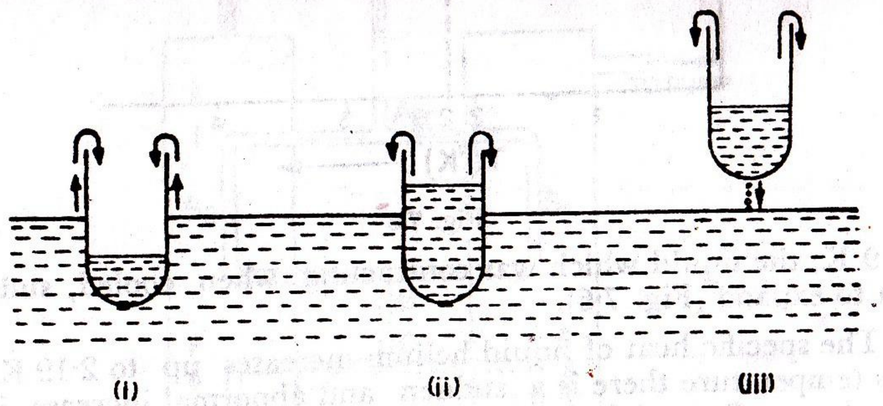


Fig. 7·8

the liquid [Fig. 7·8 (*i*)]. On the other hand when the vessel containing helium II is taken out of the liquid, it creeps out of the vessel and continues to flow until the level outside and inside is the same. [Fig. 7·8 (*ii*)]. Even when the vessel is completely out of the liquid, helium II creeps out and flows down the outer surface of the vessel [Fig. 7·8 (*iii*)]. It continues to flow until the vessel is empty.

Helium II has a higher heat of vaporization and smaller surface tension. The large specific heat anomaly of liquid helium at 2·19 K is due to rapid decrease of its entropy with decreasing temperatures. This is a complicated phenomenon and statistical mechanics cannot be applied. However, Bose-Einstein statistics can be applied in this case.

7·9 Production of Low Temperatures

Quite long ago is was noticed that there is a lower limit for a temperature scale. There is no limit for high temperatures but there is a limit for low temperature. The lowest temperature corresponds to 0 K (—273·16°C) called the absolute zero temperature. Attempts have been made to reach absolute zero temperature.

Temperatures below zero degree centigrade can be obtained with the help of freezing mixtures. Temperatures up to —65°C can be obtained with KOH and ice. With the liquefaction of gases temperatures lower than —65°C could be achieved. With liquid helium boiling under normal pressure a temperature of —268·9°C can be reached. By boiling liquid helium under reduced pressure temperature of the order of 1 K could be obtained. With liquid helium [isotope, He^3] boiling under reduced pressure a temperature of 0·4 K can be reached. Temperatures below 0·4 K can be reached by 'adiabatic demagnetisation methods' due to Debye (1926) and Giauque (1927).

7·10 Adiabatic Demagnetisation

Debye, Giauque and Macdougall were able to produce temperatures below 1 K with the help of gadolinium sulphate. Haas and Kramers used the magnetic balance for a number of paramagnetic substances. They found that potassium and chromium alum give a much lower temperature.

The apparatus used is shown in Fig. 7·9. The paramagnetic salt is suspended in a vessel, which is surrounded by liquid helium.

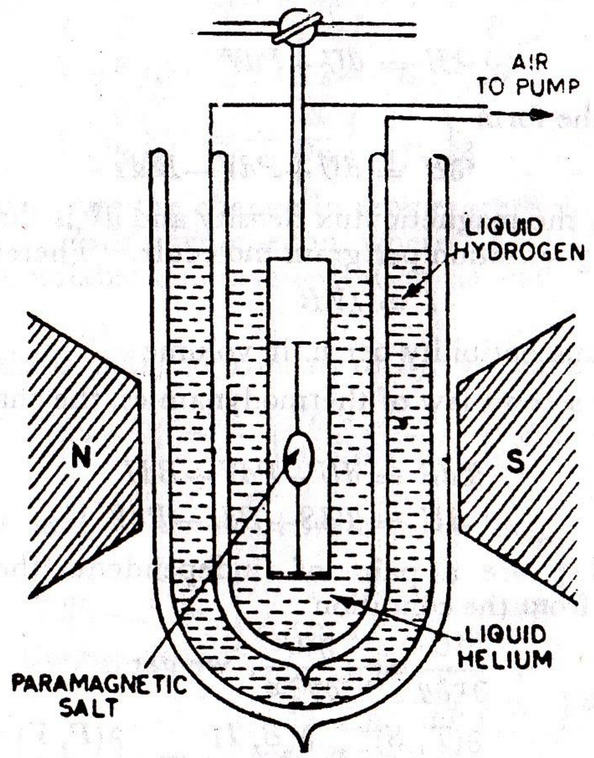


Fig. 7·9

Liquid helium is boiled under reduced pressure. It is surrounded

be a Dewar flask containing liquid hydrogen. The salt is in contact with the helium gas. A magnetic field of the order of 30,000 gauss is applied.

When the magnetic field is switched on, the temperature of the salt rises. But the heat is conducted by the helium gas rapidly and the temperature of the salt falls to the original temperature of the helium bath. The helium gas is pumped out and the salt is thermally isolated.

Now the magnetic field is switched off and the temperature of the salt falls due to adiabatic demagnetisation.

To measure the temperature of the salt, the susceptibility is measured with the help of magnetic thermometers. According to Curie's law

χT is constant

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

χ_1 is the sesceptibility at temperature T_1 of the helium bath. χ_2 is the susceptibility after adiabatic demagnetisation at temperature T_2.

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

The thermodynamical behaviour of a paramagnetic crystal, placed in a magnetic field, depends also on the strength of the magnetising field in addition to pressure and volume. The usual relation

$$\delta H = dU + PdV$$

is modified in the form

$$\delta H = dU + PdV - B.dI \qquad \ldots(i)$$

Here B is the magnetic flux density and dI is the change in the intensity of magnetisation per gram molecule. Therefore

$$I = \chi VB \qquad \ldots(ii)$$

where χ is the susceptibility per unit volume

From the second law of thermodynamics, the change in entropy is given by

$$TdS = dU + PdV - BdI$$

or
$$dU = TdS + BdI - PdV \qquad \ldots(iii)$$

If x and y are a pair of independent thermodynamical variables, then from the condition

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}, \text{ we get}$$

$$\frac{\partial(T, S)}{\partial(x, y)} + \frac{\partial(B, I)}{\partial(x, y)} = \frac{\partial(P, V)}{\partial(x, y)} \qquad \ldots(iv)$$

In the adiabatic demagnetisation experiments, the change in volume is negligible. It means $\partial V = 0$ *i.e.* V = constant.

$$\therefore \quad \frac{\partial(T, S)}{\partial(x, y)} = -\frac{\partial(B, I)}{\partial(x, y)} \qquad \ldots(v)$$

This is a general equation connecting T, S, B and I. The various thermodynamical relations can be derived by choosing any two out of these four variables T, S, B and I.

(1) Taking $x = B$ and $y = T$

$$\left(\frac{\partial S}{\partial B}\right)_T = \left(\frac{\partial I}{\partial T}\right)_B \qquad \ldots(vi)$$

(2) Taking $x = B$ and $y = S$

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial I}{\partial S}\right)_B \qquad \ldots(vii)$$

From equation (*vii*)

$$\left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial I}{\partial S}\right)_B$$

$$= -\frac{\left(\frac{\partial I}{\partial T}\right)_B}{\left(\frac{\partial S}{\partial T}\right)_B}$$

But $T\left(\frac{\partial S}{\partial T}\right)_B = C_B$, the specific heat of the substance at constant field.

$$\therefore \quad \left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial I}{\partial T}\right)_B \times \frac{T}{C_B}$$

or
$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C_B}\left(\frac{\partial I}{\partial T}\right)_B \qquad \ldots(viii)$$

Equation (*viii*) gives the change in temperature during adiabatic demagnetisation. This phenomenon, where there is change in temperature due to adiabatic demagnetisation is called **magneto-caloric effect**.

When the field is changed from B_i to B_f, we have

$$T_f - T_i = -\int_{B_i}^{B_f} \frac{T}{C_B}\left(\frac{\partial I}{\partial T}\right)_B dB \qquad \ldots(ix)$$

But $I = \chi BV$ and $\chi = \frac{C}{T}$ (from Curie law),

$$T_f - T_i = \int_{B_i}^{B_f} \frac{T}{C_B} \frac{d}{dT}(\chi BV)\, dB$$

$$= -\int_{B_i}^{B_f} \frac{TBV}{C_B} \frac{d}{dT}\left(\frac{C}{T}\right) dB$$

$$= -\int_{B_i}^{B_f} \frac{TBVC}{C_B}\left(-\frac{1}{T^2}\right) dB$$

$$= \frac{CV}{C_B T}\int_{B_i}^{B_f} B.dB \qquad \ldots(x)$$

$$\therefore \qquad T_f - T_i = \frac{CV}{C_B T} \cdot \frac{(B_f^2 - B_i^2)}{2}$$

When the magnetic field is switched off,

$$B_f = 0$$

$$T_f - T_i = -\frac{CVB_i^2}{2C_B T_i} \qquad \ldots(xi)$$

As $(T_f - T_i)$ is negative, it means there is fall in temperature due to adiabatic demagnetisation. Therefore fall in temperature,

$$\triangle T = \frac{CVB_i^2}{2\ C_B T_i} \qquad \ldots(xii)$$

7·11 Conversion of Magnetic Temperature to Kelvin Temperature

The thermodynamical behaviour of a paramagnetic crystal placed in a magnetic field is given by the relation

$$\delta H = dU + PdV - BdI$$

As the change in volume is negligible,

$$\delta H = dU - BdI \qquad \ldots(i)$$

When the magnetic field is kept zero and constant, we have

$$\theta = \left(\frac{\partial U}{\partial S}\right)_{B=0}$$

or

$$\theta = \frac{\left(\frac{\partial U}{\partial T}\right)_{B=0}}{\left(\frac{\partial S}{\partial T}\right)_{B=0}} \qquad \ldots(ii)$$

Here θ is the temperature expressed on the Kelvin scale and T is the magnetic temperature.

To determine the value of θ, the values of $\left(\frac{\partial U}{\partial T}\right)_{B=0}$ and $\left(\frac{\partial S}{\partial T}\right)_{B=0}$ are to be evaluated. It is done as follows :—

The paramagnetic substance is taken at a known initial temperature θ_i. Here θ_i is found using a helium vapour pressure thermometer.

The initial state of the substance, when $B = 0$, is represented by the point A (Fig. 7·10). The entropy at $A = S_1$. When the field is increased, keeping temperature constant, the point B_1 is reached. Let S_2 be the entropy of the substance at B_1. The quantity of heat δH produced during magnetisation is directly measured. The change in entropy $dS = S_2 - S_1 = \frac{\delta H}{\theta_i}$.

Now, the substance is adiabatically demagnetised until the field becomes zero and the point C_1 is reached. During this process there

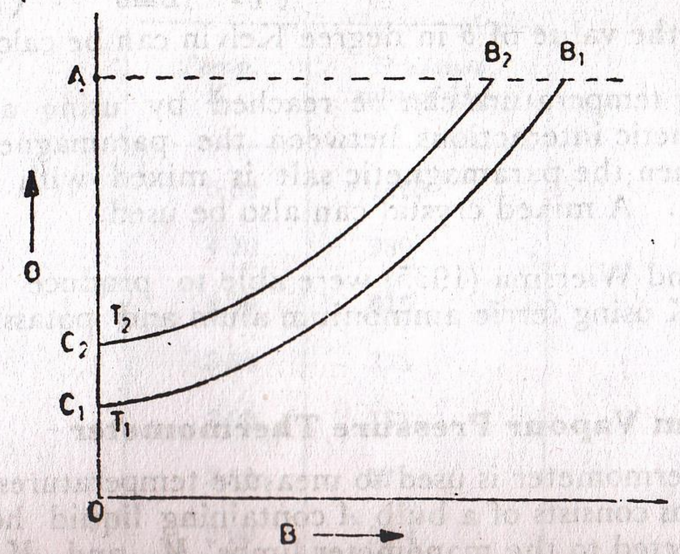


Fig. 7·10

is no change in entropy. The difference in entropy between the points C_1 and A is equal to difference in entropy between the points B_1 and A.

Suppose, the temperature at the point C_1 is θ degrees Kelvin or T degrees magnetic. The values T and $S_2 - S_1$ will depend upon the value of the magnetising field B. The experiment is repeated with different initial fields and a graph is plotted between dS and T (Fig. 7·11).

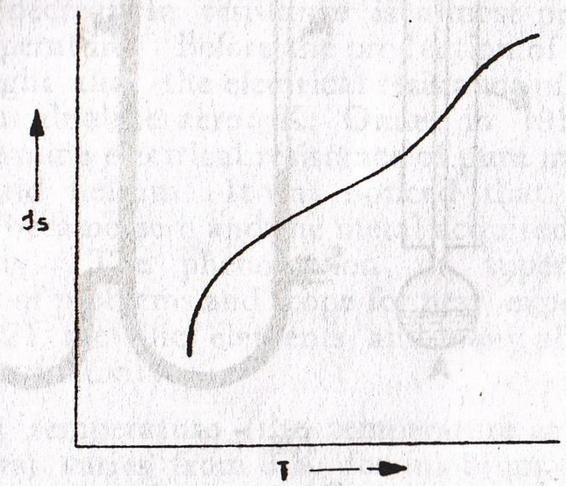


Fig. 7·11.

From this graph, the value of $\left(\frac{\partial S}{\partial T}\right)_{B=0}$ is found.

To determine the value of $\left(\frac{\partial U}{\partial T}\right)_{B=0}$, the salt is heated from a temperature T to T' and the heat absorbed is estimated directly. This can be done by introducing γ-rays or radiations from a heated filament.

Substituting the values of $\left(\frac{\partial S}{\partial T}\right)_{B=0}$ and $\left(\frac{\partial U}{\partial T}\right)_{B=0}$ in equation (*ii*) the value of θ in degree Kelvin can be calculated.

A lower temperature can be reached by using a mixed salt because magnetic interactions between the paramagnetic ions are weakened when the paramagnetic salt is mixed with a non-paramagnetic salt. A mixed crystal can also be used.

Haas and Wiersma (1935) were able to produce temperatures up to 0 003 K using ferric ammonium alum and potassium chrome alum.

7·12 Helium Vapour Pressure Thermometer

This thermometer is used to measure temperatures upto 0·7 K. The apparatus consists of a bulb *A* containing liquid helium. This bulb is connected to the manometer limbs M_1 and M_2 through a connecting tube *C*. The tube *C* is surrounded by a copper tube *B* to ensure uniform temperature of the vapour. *R* is a reservoir containing mercury (Fig. 7·12).

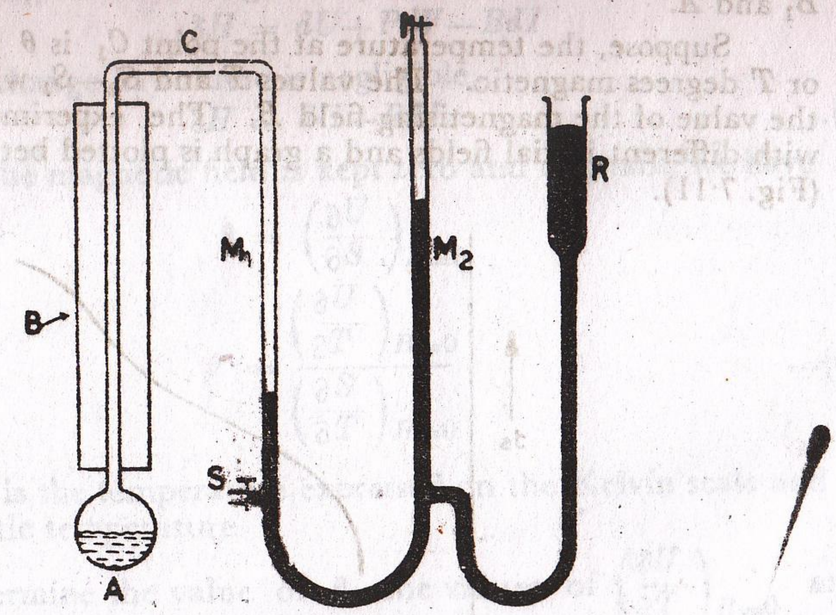


Fig. 7·12.

Initially the reservoir *R* is lowered so that the mercury in the manometers M_1 and M_2 is below the stop-cock *S*. The tube is connected to an evacuation pump to remove air in the tube *C* and the bulb *A*. The stop cock *S* is closed after evacuation and the bulb *A* is placed in the bath whose temperature is to be measured. The pressure of saturated helium vapour is measured from the difference in levels of Hg in the limbs M_1 and M_2. With the help of constant tables, giving the vapour pressure of the liquid at various temperatures, the temperature corresponding to any observed vapour pressure is determined. For lower temperatures, the graph between saturated vapour pressure and temperature is extrapolated.

Vapour preseure of Helium (He^4) at different temperature

Temp. K	*Pressure mm of* Hg
5·00	1460
4·50	980
4·00	615
3·50	353
3·00	181
2·50	77
2·00	23·4
1·50	3·6
1·00	0·12
0·50	$1·6 \times 10^{-5}$
0·10	$3·4 \times 10^{-32}$

7·13 Super-conductivity

The electrical resistance of metals decreases with decrease in temperature. The decrease in resistance is almost proportional to the decrease in temperature. Before the production of low temperatures, it was thought that the electrical resistance of a conductor becomes zero only at absolute zero. K. Onnes in 1911 performed experiments to determine electrical resistance of pure mercury at the temperature of liquid helium. It was noticed that at 4·2 K the electrical resistance became zero and the metal acquired the property of super-conductivity. The phenomenon of super-conductivity opened a new series of problems and scope for new experimentation. It was found that 21 metallic elements and many alloys show the property of super-conductivity.

The transition temperature (the temperature at which super-conductivity appears) varies from 8 K for niobium to 0·35 K for Hafnium. Niobium nitride has a transition temperature of 15·5 K. The absence of electrical resistance below the transition temperature is illustrated by the fact that a current of about 1000 amperes passed through a tin wire at about 3 K shows no heating at all. If a current is passed through a ring of lead at a temperature of 7 K (say inductively) the current circulates undiminished through the ring for a number of days.

The recent experiments on super-conductivity reveal that this property is not confined to a few metals or alloys but may be present in all metals or alloys provided they can be cooled to temperatures nearer absolute zero.

7·14 Electrolux Refrigerator

The schematic diagram of an electrolux refrigerator is shown. in Fig. 7·13.

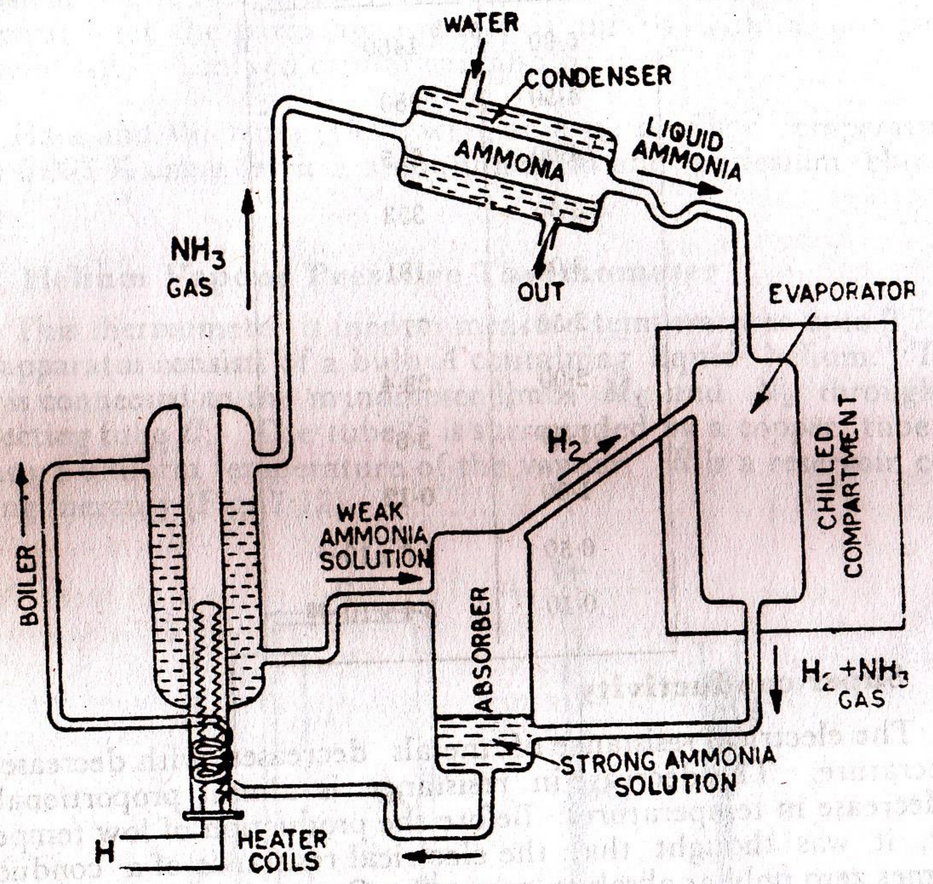


Fig. 7·13

The weak ammonia solution in the boiler is forced into the absorber. The strong ammonia solution goes into the boiler and the gaseous ammonia enters the condenser. It is cooled and is condensed. Liquid ammonia enters the evaporator and is mixed with hydrogen. Hydrogen reduces the partial pressure of ammonia below its saturation point and causes evaporation. This evaporator is surrounded by the chilled compartment. Hydrogen and gaseous ammonia leave the evaporator and enter the absorber. Here they meet the weak ammonia solution. The ammonia gas is dissolved and hydrogen gas rises through the absorber and enters the evaporator. The strong ammonia solution is forced up into the boiler again. The process continues and a sufficiently low temperature is produced in the chilled compartment. The advantage of this apparatus is that no compressor is required and the circulation of the liquid and the gas is automatic.

Exercise VII

1. Give the experimental arrangement of the cascade process for the liquefaction of oxygen. *(Punjab 1964)*

2. Describe Linde's process for the liquefaction of air. *(Lucknow 1963 ; Agra 1962 ; Delhi 19[illegible])*

3. Give the industrial process for the liquefaction of hydrogen. Explain the principle on which it is based. [*Agra 1963*]

4. Describe Claude's process for the liquefaction of air.

5. Discuss K. Onnes method for the liquefaction of helium.

6. Discuss the properties of Helium I and Helium II. What do you understand by λ-point ? Give the properties of helium II.

7. Write a short account on the production and measurement of low temperatures.

8. Describe the methods for the liquefaction of hydrogen and helium using Joule-Thomson effect. [*Panjab 1963*]

9. Describe Joule-Thomson effect and give its theory. How has it been utilised in the liquefaction of gases ?
[*Delhi 1967 ; Calcutta 1966*]

10. Describe with necessary theory, the method of adiabatic demagnetisation for producing very low temperatures. How are such temperature measured on absolute scale ? [*Delhi (Hons) 1971*]

11. Describe with necessary theory the method of producing very low temperatures by adiabatic demagnetisation. Give a method to measure such low temperatures. [*Delhi (Hons.) 1972*]

12. Describe fully one method of liquefying a gas. State clearly the principle underlying the method and explain how the temperature of liquefaction may be measured.
[*Delhi 1975*]

13. Explain the phenomenon of adiabatic demagnetisation. How will you employ this phenomenon to produce and measure very low temperatures. [*Delhi (Hons.) 1975, 76*]

14. Give an account of liquefaction of gases. Explain regenerative cooling method. [*Delhi 1976*]

15. Distinguish between adiabatic process and Joule-Thomson effect. Show that the Joule-Thomson effect is zero for a perfect gas.
[*Delhi (Hons.) 1978*]

16. Obtain an expression for the fall in temperature due to adiabatic demagnetisation in a paramagnetic gas obeying Curie's Law. [*Delhi (Hons.), 1978*]

17. Write short notes on

(*i*) Adiabatic demagnetisation
[*Berhampur 1972 ; Agra 1969 ; Delhi (Hons.) 1971*]

(*ii*) Super-conductivity [*Delhi 1972, 74*]

(*iii*) Helium vapour pressure thermometer

(*iv*) Helium II [*Delhi (Hons.) 1972, 1977*]

(*v*) Electrolux refrigerator

(*vi*) Production of low temperatures [*Panjab 1966*]

(*vii*) Liquefaction of gases
[*Berhampur 1972 ; Delhi (Sub) 1966*]

(*viii*) Approach to absolute zero. (*Delhi 1971, 73*)

8

Transmission of Heat

8·1 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 storage, 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 intervening 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.

8·2 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 θ_1 and θ_2 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

$$Q \propto A$$
$$Q \propto (\theta_1 - \theta_2)$$
$$Q \propto t$$
$$\propto \frac{1}{x}$$

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

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

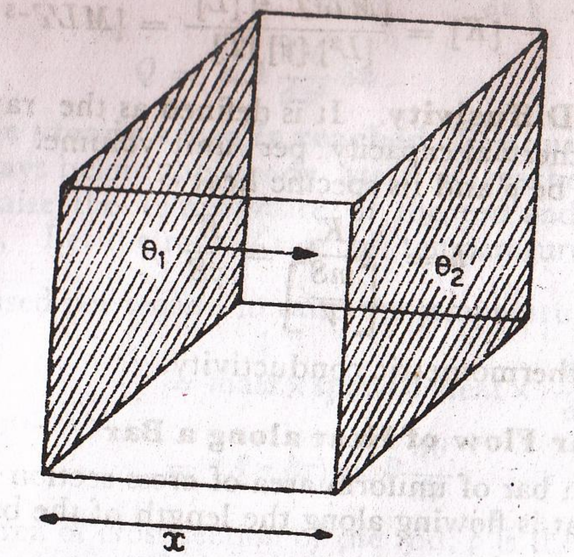


Fig. 8·1

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

If $A = 1$ sq cm, $(\theta_1 - \theta_2) = 1°C$, $t = 1$ s, $x = 1$ 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 $\frac{d\theta}{dx}$

represents the rate of change of temperature with respect to the distance. As temperature decreases with increase in distance from the hot end, the quantity $\frac{d\theta}{dx}$ is negative and is called the temperature gradient.

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

Dimensions of K

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

Q represents energy and its dimensions are,

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

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

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

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.

8·3 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

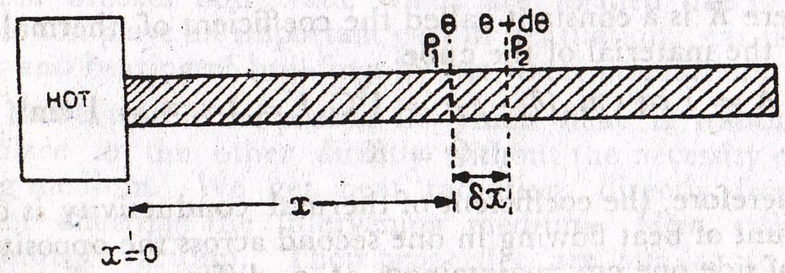


Fig. 9·2

planes P_1 and P_2 perpendicular to the length of 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

$$Q_1 = -KA\,\frac{d\theta}{dx} \qquad \ldots(i)$$

Heat flowing through P_2 in one second

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

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

$$Q = Q_1 - Q_2$$

$$= -KA\frac{d\theta}{dx} + KA\,\frac{d}{dx}\left(\theta + \frac{d\theta}{dx}\delta x\right)$$

$$Q = KA\,\frac{d^2\theta}{dx^2}\delta x \qquad \ldots(iii)$$

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

$$= \text{mass} \times \text{specific heat} \times \frac{d\theta}{dt}$$

$$= (A \times \delta x)\rho \times S\,\frac{d\theta}{dt} \qquad \ldots(iv)$$

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

$$= Ep\,\delta\,x\,\theta \qquad \ldots(v)$$

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.

$$\therefore \qquad Q = A\delta x\rho \times S\,\frac{d\theta}{dt} + Ep.\delta x.\theta$$

Substituting the value of Q from equation (iii)

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

or

$$\frac{d^2\theta}{dx^2} = \frac{\rho S}{K}\,\frac{d\theta}{dt} + \frac{Ep}{KA}\,\theta \qquad \ldots(vi)$$

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)

$$\frac{d^2\theta}{dx^2} = \frac{\rho S\, d\theta}{K\, dt} = \frac{1}{h}\frac{d\theta}{dt} \qquad \ldots(vii)$$

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 stage,

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

From equation (vi)

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

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

$$\frac{d^2\theta}{dx^2} = \mu^2\theta \qquad \ldots(viii)$$

The general solution of this equation is

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

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.

At $x = 0, \quad \theta = \theta_0$

From equation (ix)

$$\theta_0 = A + B$$

At $x = \infty, \ \theta = 0$

From equation (ix),

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

But e^{∞} cannot be zero, therefore

$$A = 0$$

Taking $A = 0$

$$\theta_0 = B$$

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

$$\theta = \theta_0 e^{-\mu x} \qquad \ldots(x)$$

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

At $x = 0$

$$\theta = \theta_0$$

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

The values of A and B in this case are

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

and

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

The solution of equation (ix) will be

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

8·4 Ingen-Hausz Experiment

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

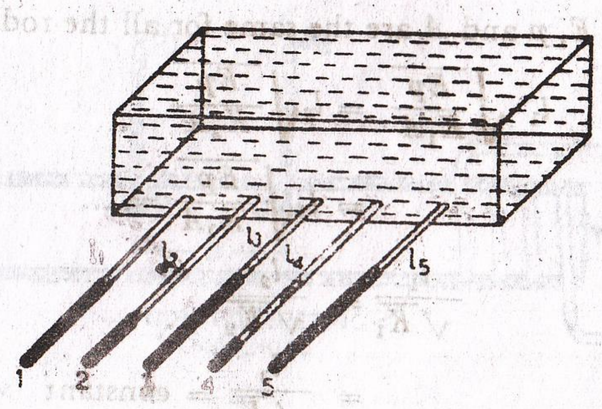


Fig. 8·3

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. 8·3) and their portions outside the vessel are coated uniformly with wax. Hot water or oil is put into the vessel and the wax starts melting. It is found that the wax melts up to different lengths on different rods.

Let the lengths up to which the wax has melted be l_1, l_2, l_3.... 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 temperature.

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,

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

.....

$$\therefore \quad \theta_m = \theta_0 e^{-\mu_1 l_1} = \theta_0 e^{-\mu_2 l_2} = \theta_0 e^{-\mu_3 l_3}$$

$$\therefore \quad \mu_1 l_1 = \mu_2 l_2 = \mu_3 l_3 = \ldots$$

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

$$\therefore \quad l_1\sqrt{\frac{Ep}{K_1 A}} = l_2\sqrt{\frac{Ep}{K_2 A}} = l_3\sqrt{\frac{Ep}{K_3 A}} = \ldots$$

$$\therefore \quad \frac{l_1}{\sqrt{K_1}} = \frac{l_2}{\sqrt{K_2}} = \frac{l_3}{\sqrt{K_3}} = \text{constant}$$

or $$\frac{K_1}{l_1^2} = \frac{K_2}{l_2^2} = \frac{K_3}{l_3^2} = \text{constant} \qquad \ldots(i)$$

Thus, the thermal 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.

Example 8·1. *In an Ingen-hausz experiment, wax melted over 10* cm *of copper rod and over 4* cm *of iron rod. What is the conductivity of iron when the conductivity of copper is 0·90 ?*

Here, $l_1 = 10$ cm

$l_2 = 4$ cm

$K_1 = 0{\cdot}90$

$K_2 = ?$

$$\frac{K_2}{K_1} = \frac{l_2^2}{l_1^2}$$

$$K_2 = \frac{l_2^2}{l_1^2} \times K_1$$

$$= \frac{16}{100} \times 0{\cdot}90$$

$$K_2 = \mathbf{0{\cdot}144}$$

8·5 Searle's Method

XY is a rod whose coefficient of thermal conductivity is to be determined. The end X is enclosed in a steam jacket and steam is continuously passed through it. Heat is conducted along the rod and when the steady state is reached, the thermometers θ_1, θ_2, θ_3 and θ_4 record constant temperatures. The mass of water (m grams) collected in a known interval of time (t seconds) is noted (Fig. 8·4).

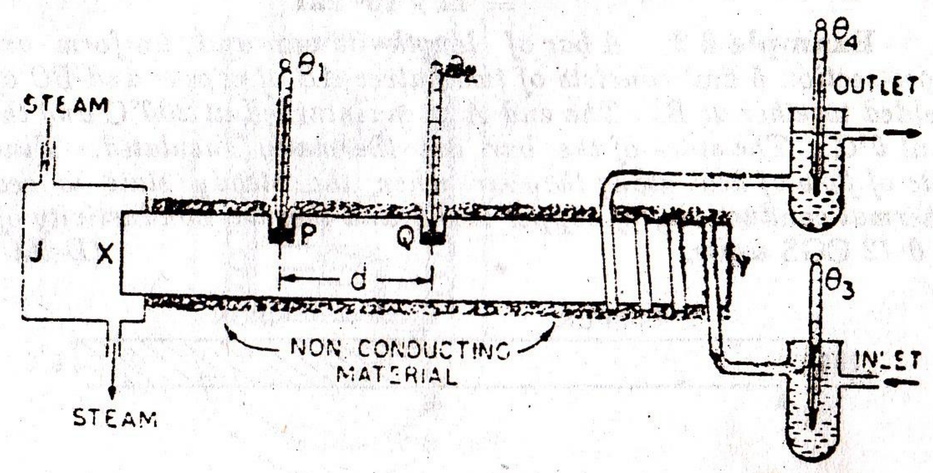


Fig. 8·4.

When the steady state is reached, the quantity of heat passing from the section P to Q is constant and the same quantity of heat

flows through the section at Y. The rod is well covered with a non-conducting material like felt, cotton etc. to avoid conduction and convection of heat to the atmosphere.

Quantity of heat that flows from the section at P to Q in one second,

$$= \frac{KA(\theta_1-\theta_2)\times 1}{d} \quad \ldots(i)$$

Amount of heat gained by water in one second

$$= \frac{m(\theta_4-\theta_3)}{t} \quad \ldots(ii)$$

Equating (i) and (ii)

$$\frac{KA(\theta_1-\theta_2)}{d} = \frac{m(\theta_4-\theta_3)}{t}$$

$$\therefore \quad K = \frac{md(\theta_4-\theta_3)}{At(\theta_1-\theta_2)}$$

Knowing all the quantities, K can be calculated.

Example 8·2. *The opposite faces of a metal plate of 0·2 cm thicknsss are at a difference of temperature of 100°C and the area of the plate is 200 sq cm. Find the quantity of heat that will flow through the plate in one minute if* K = *0 2 CGS units.*

Here
$$K = 0{\cdot}2$$
$$A = 200 \text{ sq cm}$$
$$d = 0{\cdot}2 \text{ cm}$$
$$(\theta_1-\theta_2) = 100°\text{C}$$
$$t = 60 \text{ s}$$
$$Q = \frac{KA(\theta_1-\theta_2)\,t}{d}$$
$$= \frac{0{\cdot}2\times 200\times 100\times 60}{0{\cdot}2}$$
$$= \mathbf{12\times 10^5 \text{ cal}}$$

Example 8 3. *A bar of length 30 cm and uniform area of cross-section 5 cm² consists of two halves AB of copper and BC of iron welded together at B. The end A is maintained at 200°C and the end C at 0°C. The sides of the bar are thermally insulated. Find the rate of flow of heat along the bar when the steady state is reached. Thermal conductivity of copper is 0·9 and thermal conductivity of iron is 0·12 CGS units.* (*Delhi 1973*)

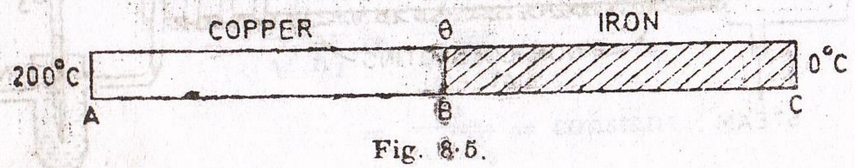


Fig. 8·5.

Suppose the temperature at the interface B is θ after the steady state is reached.

$$\therefore \quad \frac{K_1A(200-\theta)}{d} = \frac{K_2A(\theta-0)}{d}$$

$$0{\cdot}9(200-\theta) = 0{\cdot}12\,\theta$$
$$\theta = 176{\cdot}5°\text{C}$$

After the steady state is reached, the rate of flow of heat is the same in both the bars.

$$\therefore \quad Q = \frac{K_1A(\theta_1-\theta)}{d}$$

$$Q = \frac{0{\cdot}9\times 5\times(200-176{\cdot}5)}{15}$$

or $$Q = \mathbf{7{\cdot}05 \text{ cal/s}}$$

Example 8·4. *An ice box is built of wood 1·75* cm *thick, lined inside with cork 3* cm *thick. If the temperature of the inner surface of the cork is 0°C and that of the outer surface of wood is 12°C, what is the temperature of the interface ? The thermal conductivity of wood and cork are 0·0006 and 0·00012* CGS *units respectively.* [*Delhi, 1975*]

Suppose the temperature of the interface is θ after the steady state is reached

$$\therefore \quad \frac{K_1A(12-\theta)}{d_1} = \frac{K_2A(\theta-0)}{d_2}$$

Here
$$K_1 = 0{\cdot}0006,\ K_2 = 0{\cdot}00012$$
$$d_1 = 1{\cdot}75 \text{ cm},\ d_2 = 3 \text{ cm}$$

$$\frac{0{\cdot}0006(12-\theta)}{1{\cdot}75} = \frac{0{\cdot}00012(\theta)}{3}$$

$$\theta = \mathbf{10{\cdot}74°\text{C}}$$

8·6. Lee's Method for Metals

The thermal conductivity of a metal is different at different temperatures. This method is useful in measuring the thermal

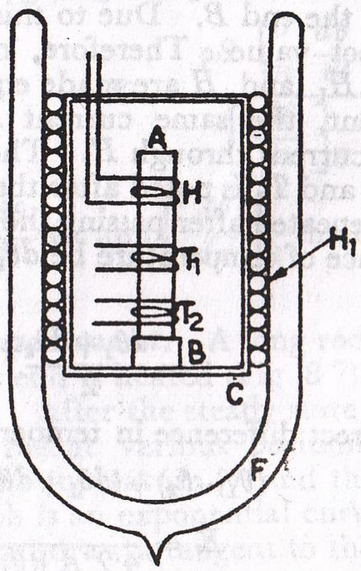


Fig. 8·6

conductivity of a metal at various temperatures, preferably at low temperatures.

The apparatus consists of a copper frame C surrounded by a heating coil H_1. The specimen rod AB about 10 cm long and 0·5 cm in diameter is fitted inside the frame C (Fig. 8·6). The end A of the rod is heated by a heating coil H and T_1 and T_2 are two platinum resistance thermometers. These thermometers measure temperatures at the two points distant d apart on the rod AB. The end B is fixed in a socket inside the frame C. The whole arrangement is surrounded by a Dewar flask F.

The whole apparatus is immersed in liquid air so that its temperature is below the temperature at which the thermal conductivity is to be measured. The liquid air is removed and with the help of the heating coil H_1 the whole apparatus is brought to the desired temperature. The heating coil H is heated by passing a knowing current through it and the temperatures of T_1 and T_2 are noted, after they show constant temperatures, θ_1 and θ_2 *i.e.*, after the steady state has been reached. Let the current flowing be I amperes and potential difference across the heating coil H be E volts.

$$\text{Heat produced per second} = \frac{EI}{4{\cdot}2} \text{ calories}$$

$$\therefore \quad \frac{EI}{4{\cdot}2} = \frac{KA\,(\theta_1-\theta_2)}{d}$$

$$K = \frac{EId}{4{\cdot}2\,A\,(\theta_1-\theta_2)} \qquad \ldots(i)$$

Hence, the thermal conductivity of the given metal at a desired temperature can be calculated.

Correction. When the end A of the rod AB is heated by the heating coil H, the copper frame conducts some heat and its temperature rises. This heat does not escape and there is backward flow of heat from the end B. Due to this reason, $(\theta_1-\theta_2)$ will be less than the correct value. Therefore, correction is a necessity. The resistances of H_1 and H are made equal. Before performing the main experiment, the same current I is passed through H_1, without passing the current through H. The difference of temperature $d\theta_1$ between T_2 and T_1 is noted after the steady state is reached. The observation is repeated after passing the same current I through H. Let the difference of temperature be $d\theta_2$. The correction to be applied

$$= \frac{d\theta_1+d\theta_2}{2}$$

Hence the correct difference in temperature is

$$(\theta_1-\theta_2)+(d\theta_1+d\theta_2)/2$$

$$K = \frac{EId}{4{\cdot}2\,A\,[(\theta_1-\theta_2)+(d\theta_1+d\theta_2)/2]}$$

Lee found K for various metals between —170°C and 18°C. For silver, copper, zinc and aluminium K increases with rise in temperature between —170°C and 100°. For iron and lead, K decreases with rise in temperature. This method is very useful in finding the thermal conductivity of metals at different temperatures.

8·7 Forbes' Method to find K

Forbes' method is used to determine the *absolute* conductivity of different metals.

Consider a long rod of uniform area of cross-section heated at one end (Fig. 8·7). After the steady state is reached, the amount

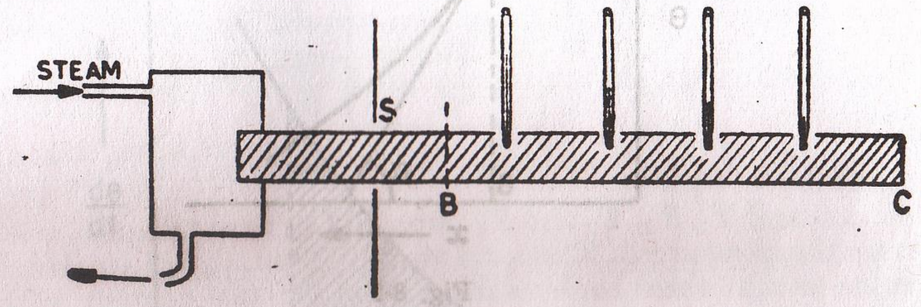


Fig. 8·7.

of heat passing per second across the cross-section at the point $B = KA\left(\frac{d\theta}{dx}\right)_B$. Here $\left[\frac{d\theta}{dx}\right]_B$ is the temperature gradient at B. The amount of heat lost by radiation from the point B up to the end C

$$= \int_B^C (\rho\, A\, dx)\, S\, \frac{d\theta}{dt}$$

$$\therefore \quad KA\left[\frac{d\theta}{dx}\right]_B = \int_B^C (\rho\, A\, dx)\, S\, \frac{d\theta}{dt}$$

$$K = \frac{\rho S \int_B^C \frac{d\theta}{dt}\, dx}{\left[\frac{d\theta}{dx}\right]_B} \qquad \ldots(i)$$

To find $\int_B^C \frac{d\theta}{dt}\, dx$ and $\left[\frac{d\theta}{dx}\right]_B$ the experiment is divided into two parts.

(*i*) **Static Experiment.** A long rod about 2 metres in length is taken and its one end is heated (Fig. 8·7). Forbes heated the rod for about six hours. After the steady state is reached, the thermometers fixed in the rod at various positions are read. A graph is plotted between the temperature (θ) and the distance (x) from the hot end. The graph is an exponential curve as shown in Fig. 8.8. Take the point B and draw a tangent to the curve corresponding to the point B.

Here $\left[\frac{d\theta}{dx}\right]_B = \tan\alpha$

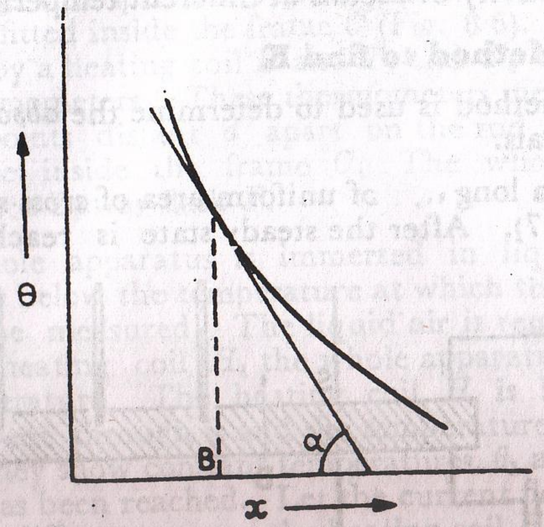


Fig. 8·8

(ii) Dynamic Experiment. The original bar or a small bar of the same material having the same area of cross-section is heated to the temperature of steam. The bar is exposed to the atmosphere and a thermometer is fixed at its middle portion (Fig. 8·9). Note the.

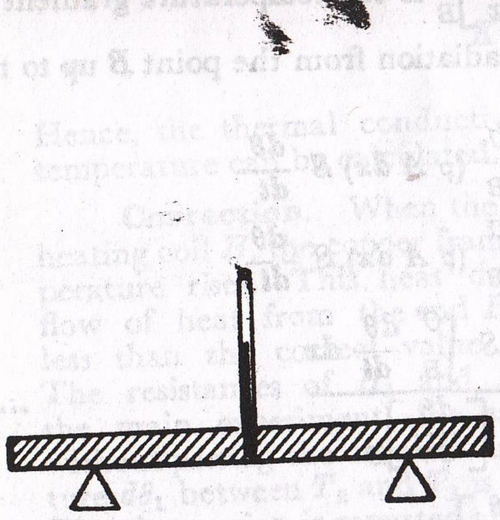


Fig. 8·9

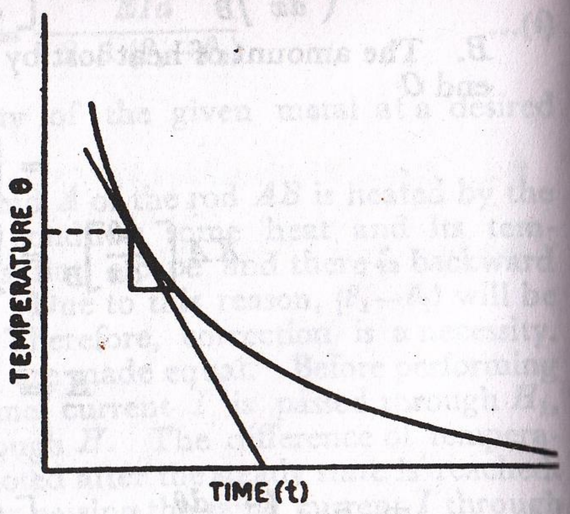


Fig. 8·10

temperature of the bar after regular intervals of time (say one minute). Draw a graph between temperature and time.

From the graph in Fig. 8·10, for various values of θ, $\frac{d\theta}{dt}$, is determined. This is done by drawing tangents to the curve at various points on the curve.

From the two graphs given in Figs. 8·8 and 8·10, the values of $\frac{d\theta}{dt}$, corresponding to θ and x are determined. A graph is plotted

between $\frac{d\theta}{dt}$ and x. The graph is produced to meet the x-axis. Corresponding to the point B, a point is located on the graph (Fig. 8·11). The area of the shaded portion $= \int_B^C \frac{d\theta}{dt}\, dx$. The area is measured with the help of the planimeter or from the graph directly.

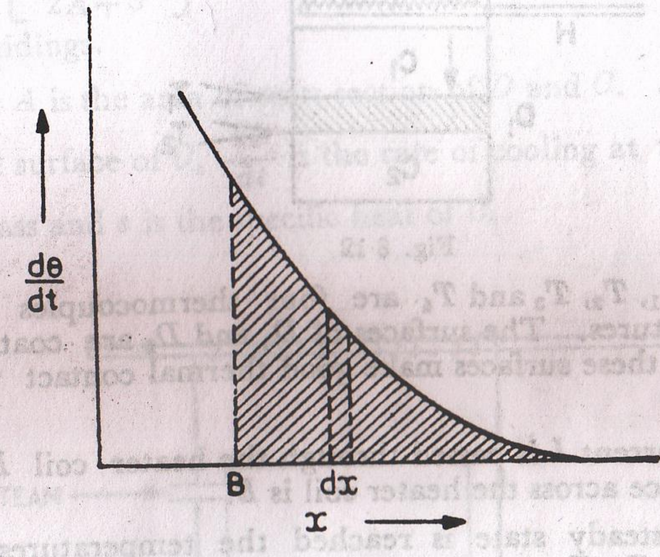


Fig. 8·11

$$K = \frac{\rho S \int_B^C \frac{d\theta}{dt}.dx}{\left[\frac{d\theta}{dx}\right]_B}$$

$$K = \frac{\rho S \text{ (area of the shaded portion)}}{\tan\alpha}$$

Hence K can be calculated.

This method is tedious because it takes a long time and three graphs are to be drawn. Moreover, the specific heat S does not remain constant at all temperatures. Also the distribution of heat is not the same along the bar in the two experiments. Therefore, this experiment is not accurate. But the advantage of this experiment is that the absolute conductivity of the material of the rod can be determined.

8·8 Lee's Method for Bad Conductors

This method is used to determine the thermal conductivity of poor conductors *viz.*, rubber, glass, ebonite, wood, cork etc. The specimen is taken in the form of two thin discs D_1 and D_2 about 10 cm in diameter and 2 to 3 mm thick. The disc D_1 is pressed between two copper plates C_1 and C_2 and D_2 is pressed between the

copper plates C_3 and C_4 (Fig. 8·12). Discs C_1 and C_3 ensure normal flow of heat through the experimental plates D_1 and D_2. H is a

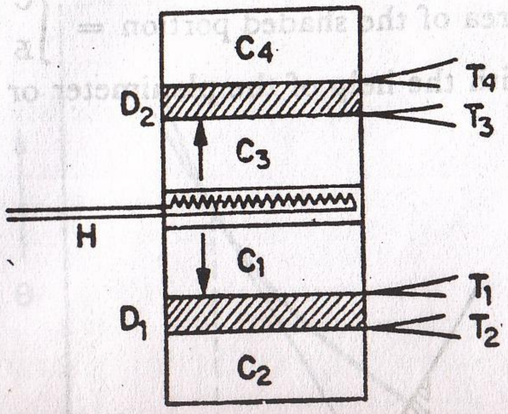


Fig. 8·12

heater coil and T_1, T_2, T_3 and T_4 are four thermocouples used to measure temperatures. The surfaces of D_1 and D_2 are coated with glycerine so that these surfaces make good thermal contact with the copper plates.

A steady current I is passed through the heater coil H. The potential difference across the heater coil is E.

After the steady state is reached the temperatures of the thermometers T_1, T_2, T_3 and T_4 are noted. Let the temperatures be θ_1, θ_2, θ_3 and θ_4 respectively. In the steady state, heat generated in the heater coil is lost from the surface of C_3 and C_4, and heat lost from the rims of C_1, C_2, D_1 and D_2 is negligible due to the small thickness of the plates.

Let d_1 be the thickness of the disc D_1 and d_2 the thickness of the disc D_2.

Heat produced by heater coil in one second

$$= \frac{EI}{4{\cdot}2} \text{ calories} \qquad \ldots(i)$$

Heat passing through D_1 and D_2 in one second

$$= \frac{KA\,(\theta_1-\theta_2)}{d_1} + \frac{KA\,(\theta_3-\theta_4)}{d_2} \qquad \ldots(ii)$$

Equating (i) and (ii)

$$\frac{EI}{4{\cdot}2} = \frac{KA\,(\theta_1-\theta_2)}{d_1} + \frac{KA\,(\theta_3-\theta_4)}{d_2} \qquad \ldots(iii)$$

The value of K is calculated from equation (iii).

8·9 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. 8·13). 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.

$$\therefore \quad \frac{KA\,(\theta_1-\theta_2)}{d} = ms\,\frac{d\theta}{dt}\left[\frac{A+S}{2A+S}\right] \qquad \ldots(i)$$

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.

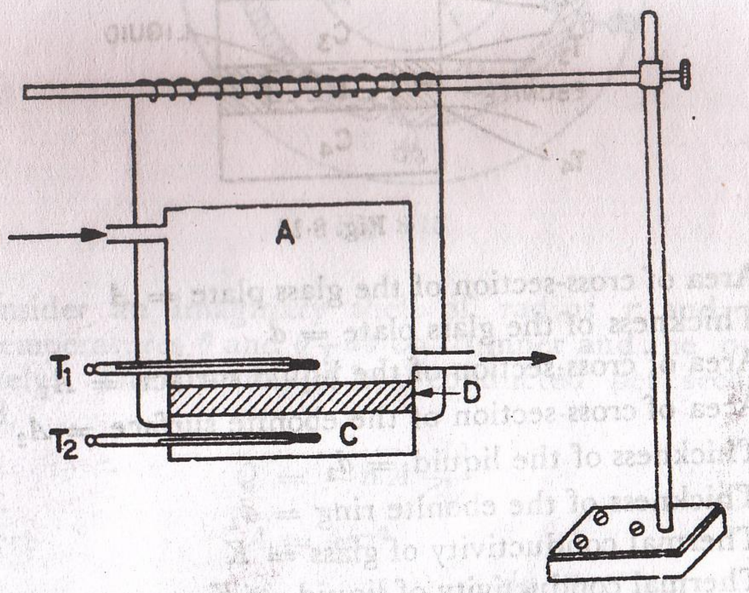


Fig. 8·13

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°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.

8·10 Lee's Method for Liquids

To determine the thermal conductivity of a liquid, convection current should be determined. To overcome this difficulty, heat should flow from the upper surface to the lower surface of the liquid.

Lee designed an apparatus shown in Fig. 8·14. C_1, C_2, C_3 and C_4 are the copper plates of uniform thickness. H is the heater coil. A glass plate is pressed between C_2 and C_3. The thermocouples T_1, T_2, T_3 and T_4 are used to determine the temperatures. The liquid is contained in a cylindrical tube having an ebonite ring.

A steady current of I amperes is passed through the heater coil H. After the steady state is reached, the temperatures shown by the thermocouples are noted. Let these temperatures be θ_1, θ_2, θ_3 and θ_4.

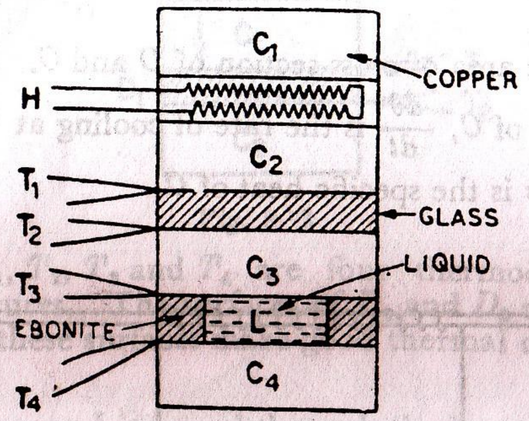


Fig. 8·14

Area of cross-section of the glass plate $= A$
Thickness of the glass plate $= d$
Area of cross-section of the liquid surface $= A_1$
Area of cross-section of the ebonite surface $= A_2$
Thickness of the liquid $= d_1$
Thickness of the ebonite ring $= d_1$
Thermal conductivity of glass $= K$
Thermal conductivity of liquid $= K_1$
Thermal conductivity of ebonite $= K_2$
Heat flowing per second through the glass plate

$$= \frac{KA\,(\theta_1-\theta_2)}{d} \qquad \ldots(i)$$

Heat flowing per second through the liquid and the ebonite ring

$$= \frac{K_1A_1\,(\theta_3-\theta_4)}{d_1} + \frac{K_2A_2\,(\theta_3-\theta_4)}{d_1} \qquad \ldots(ii)$$

Equating (*i*) and (*ii*)

$$\therefore \quad \frac{KA\,(\theta_1-\theta_2)}{d} = \frac{K_1A_1(\theta_3-\theta_4)}{d_1} + \frac{K_2A_2(\theta_3-\theta_4)}{d_1} \qquad \ldots(iii)$$

The value of K, for the liquid can be calculated from equation (*iii*). However, there is small error due to the heat lost by the sides of C_1, C_2, C_3, C_4, the glass plate and the ebonite ring.

8·11 Spherical Shell Method (Radial Flow of Heat)

Consider two thin spherical shells A and B of radii r_1 and r_2. The specimen is contained between these two shells A and B (Fig. 8·15). A heating element is placed at the centre of the shells. Heat is conducted through the specimen from the inner to the outer shell. Let the temperatures of the inner and the outer shells be θ_1 and θ_2, after the steady state is reached.

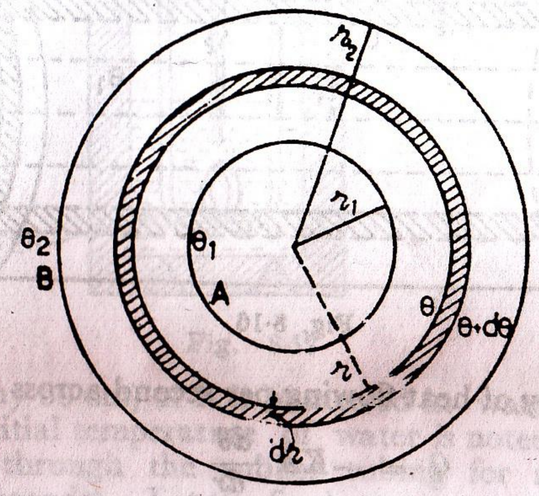


Fig. 8·15

Consider an imaginary shell of radius r and thickness dr having temperatures θ and $\theta+d\theta$ on its inner and the outer surfaces respectively. The quantity of heat conducted per second through this shell,

$$Q = -KA\frac{d\theta}{dr} \qquad \ldots(i)$$

Here $A = 4\pi r^2$

$$\therefore \quad Q = -K \cdot 4\pi r^2 \frac{d\theta}{dr}$$

$$\frac{dr}{r^2} = -\frac{4\pi K}{Q}\,d\theta$$

Integrating,

$$\int_{r_1}^{r_2} \frac{dr}{r^2} = -\frac{4\pi K}{Q}\int_{\theta_2}^{\theta_2} d\theta$$

$$\frac{1}{r_1} - \frac{1}{r_2} = \frac{4\pi K\,(\theta_1-\theta_2)}{Q}$$

$$K = \frac{Q(r_2-r_1)}{4\pi\, r_1r_2\,(\theta_1-\theta_2)} \qquad \ldots(ii)$$

K is calculated from equation (*ii*).

8·12 Cylindrical Flow of Heat

Consider a cylindrical tube of length l, inner radius r_1 and outer radius r_2. After the steady state is reached, the temperature on

the inner surface is θ_1 and on the outer surface it is θ_2. Here $\theta_1 > \theta_2$. Heat is conducted radially across the wall of the tube. Consider an element of thickness dr and length l at a distance r from the axis (Fig. 8·16).

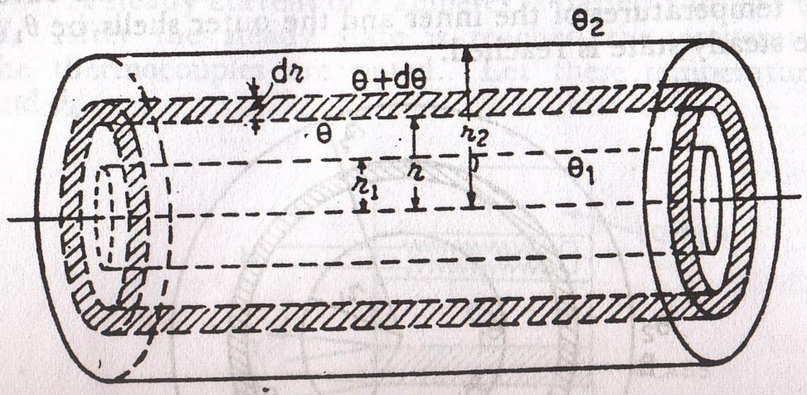


Fig. 8·16

The quantity of heat flowing per second across the element

$$Q = -KA \frac{d\theta}{dr}$$

But $$A = 2\pi rl$$

$$\therefore \quad Q = 2\pi Krl \frac{d\theta}{dr}$$

$$\frac{dr}{r} \cdot Q = -2\pi Kl \, d\theta \qquad \ldots(i)$$

Q is constant after the steady state is reached.

Integrating equation (i)

$$Q \int_{r_1}^{r_2} \frac{dr}{r} = -2\pi Kl \int_{\theta_1}^{\theta_2} d\theta$$

$$Q \left[\log_e \frac{r_2}{r_1} \right] = -2\pi Kl \, [\theta_2 - \theta_1]$$

$$Q \log_e \frac{r_2}{r_1} = 2\pi Kl \, [\theta_1 - \theta_2]$$

$$K = \frac{Q \log_e \frac{r_2}{r_1}}{2\pi l \, (\theta_1 - \theta_2)} \qquad \ldots(ii)$$

or

$$K = \frac{Q \times 2{\cdot}3026 \times \log_{10} \frac{r_2}{r_1}}{2\pi l \, (\theta_1 - \theta_2)} \qquad \ldots(iii)$$

8·13 Thermal Conductivity of Rubber

The coefficient of thermal conductivity of a rubber tubing can be determined in the laboratory applying the principle of cylindrical flow of heat.

A known quantity of water is taken in a calorimeter C. A rubber tubing whose inner and outer radii are r_1 and r_2, is taken and

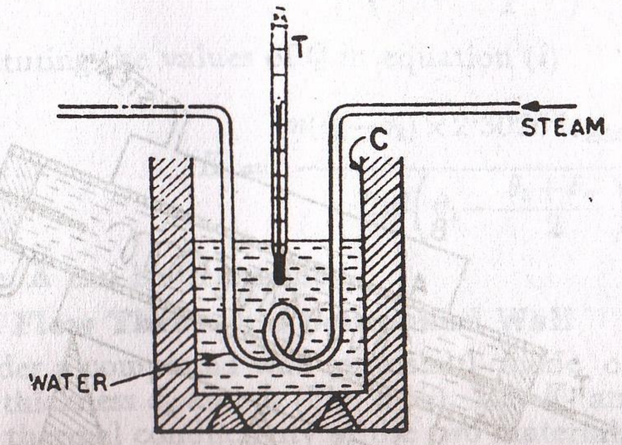


Fig. 8·17

a known length (say 50 cm) of it is immersed in water as shown in Fig. 8·17. The initial temperature of water is noted. Let it be θ_3. Steam is passed through the rubber tubing for a known time t seconds (say 900 seconds). Let the final temperature of water be θ_4 (after applying radiation correction) and temperature of steam be θ_1. The average temperature on the outer surface of the rubber tubing

$$= \theta_2 = \frac{\theta_3 + \theta_4}{2}$$

Suppose, mass of water $= m$

Water equivalent of the calorimeter $= w$

Rise in temperature $= (\theta_4 - \theta_3)$

Heat gained by water $= (m+w)\,(\theta_4 - \theta_3)$

Quantity of heat flowing per second

$$Q = \frac{(m+w)\,(\theta_4 - \theta_3)}{t}$$

But $$K = \frac{Q \times 2{\cdot}3026 \times \log_{10} \left(\frac{r_2}{r_1} \right)}{2\pi l \, (\theta_1 - \theta_2)}$$

Substituting the values of θ_2 and Q

$$K = \frac{(m+w)\,(\theta_4 - \theta_3) \times 2{\cdot}3026 \times \log_{10} \left(\frac{r_2}{r_1} \right)}{2\pi l \left(\theta_1 - \frac{\theta_3 + \theta_4}{2} \right) t}$$

Thus, K for rubber can be calculated.

8·14 Thermal Conductivity of Glass

A glass tube whose inner and outer radii are r_1 and r_2 respectively is fixed inside an outer jacket (Fig. 8·18). The apparatus is kept in the slanting position and water is allowed to flow inside the

glass tube from lower to the upper end. The thermometers T_1 and T_2 are used to determine the temperature of incoming and outgoing water. The rate of flow of water can be adjusted with the help of a pinch cock.

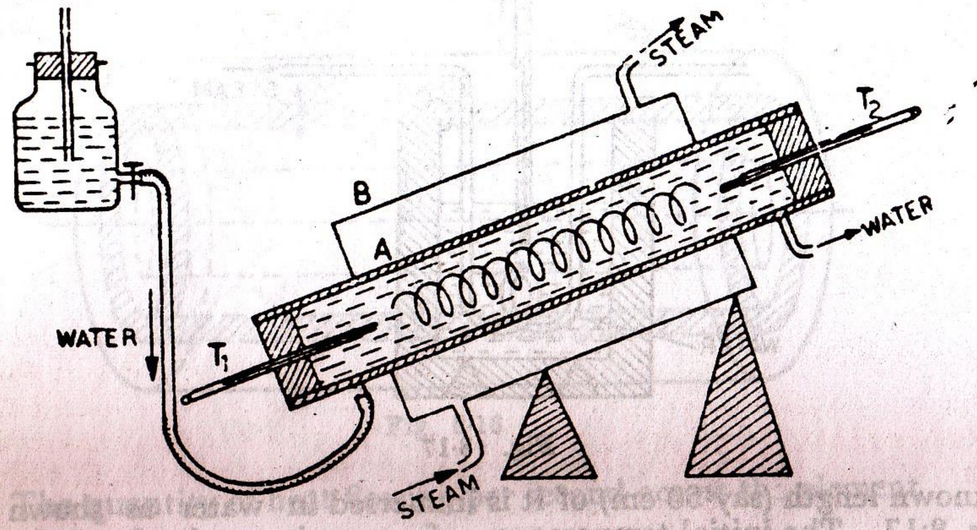


Fig. 8·18

Steam is passed inside the outer jacket and the rate of flow of water is adjusted such that the two thermometers show sufficient difference of temperature (say 5 to 10°C). When the two thermometers show constant temperature, water flowing through the glass tube for a known time t seconds (say 900 seconds) is collected in a beaker. The spiral wire inside the glass tube helps in making good contact of water with the wall of the tube.

Suppose,

Length of the tube inside the jacket $= l$

Temperature of steam $= \theta_1$

Temperature of incoming water $= \theta_3$

Temperature of outgoing water $= \theta_4$

Mass of water collected $= m$

Time taken $= t$ seconds

Quantity of heat gained by water in t seconds

$$= m\,(\theta_4 - \theta_3)$$

Quantity of heat that flows in one second across the wall of the tube,

$$Q = \frac{m\,(\theta_4 - \theta_3)}{t}$$

Average temperature of the inside of the glass tube

$$= \theta_2 = \frac{\theta_3 + \theta_4}{2}$$

But
$$K = \frac{Q \times 2{\cdot}3026 \times \log_{10}\left(\frac{r_2}{r_1}\right)}{2\pi l\left(\theta_1 - \frac{\theta_3 + \theta_4}{2}\right)} t \qquad \ldots(i)$$

Substituting the values of Q in equation (i)

$\therefore$
$$K = \frac{m(\theta_4 - \theta_3) \times 2{\cdot}3026 \log_{10}\left(\frac{r_2}{r_1}\right)}{2\pi l\left(\theta_1 - \frac{\theta_3 + \theta_4}{2}\right) t} \qquad \ldots(ii)$$

Hence, K can be determined.

8·15 Heat Flow Through a Compound Wall

Consider a compound wall (or a slab) made of two materials A and B of thickness d_1 and d_2 (Fig. 8·19). Let K_1 and K_2 be the coefficients of thermal conductivity of the two materials. θ_1 and θ_2 are the temperatures of the end faces ($\theta_1 > \theta_2$) and θ is the temperature of the surface in contact. After the steady state is reached, the heat flowing per second (Q) across any cross-section is the same.

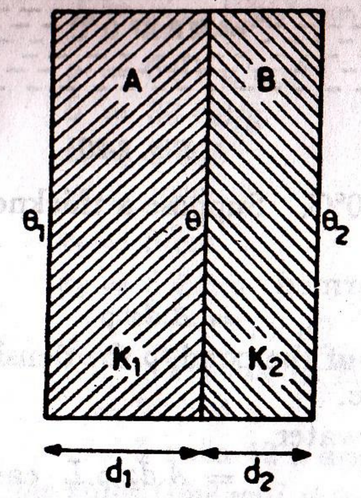


Fig. 8·19

For the material A,

$$Q = \frac{K_1 A(\theta_1 - \theta)}{d_1} \qquad \ldots(i)$$

For the meterial B,

$$Q = \frac{K_2 A\,(\theta - \theta_2)}{d_2} \qquad \ldots(ii)$$

From equations (i) and (ii),

$$\frac{K_1 A\,(\theta_1 - \theta)}{d_1} = \frac{K_2 A\,(\theta - \theta_2)}{d_2}$$

$$\theta = \frac{\frac{K_1\theta_1}{d_1} + \frac{K_2\theta_2}{d_2}}{\frac{K_1}{d_1} + \frac{K_2}{d_2}}$$

Substituting the value of θ in equation (*i*),

$$Q = \frac{A(\theta_1 - \theta_2)}{\frac{d_1}{K_1} + \frac{d_2}{K_2}} \quad \ldots(iii)$$

In general, for any number of walls or slabs,

$$Q = \frac{A(\theta_1 - \theta_2)}{\sum\left(\frac{d}{K}\right)} \quad \ldots(iv)$$

8·16 Accretion of Ice on Ponds

Consider a layer of ice x cm thick on the surface of a pond. Let the temperature of air over the surface of ice be $-\theta$°C and that

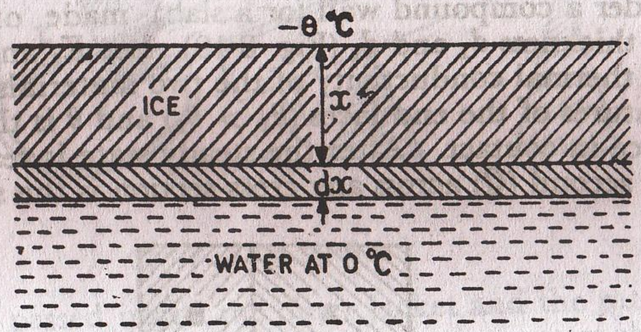


Fig. 8·20

of water below ice 0°C. Suppose a thickness dx of ice is formed in time dt (Fig. 8·20).

Mass of ice formed

$$= A.dx.\rho$$

Here A is the area of the pond, ρ the density of ice and L the latent heat of fusion of ice.

Heat lost by water

$$= A.dx.\rho.L \text{ calories} \quad \ldots(i)$$

This heat is conducted across a layer of ice of thickness x upwards.

$$\text{Heat conducted} = KA.\frac{\theta}{x}\,dt \text{ calories} \quad \ldots(ii)$$

Equating (*i*) and (*ii*)

$$KA\frac{\theta}{x}\,dt = A\,dx.\rho.L$$

$$\frac{dx}{dt} = \frac{K\theta}{\rho L x} \quad \ldots(iii)$$

$\frac{dx}{dt}$ represents the rate of growth of the thickness of ice.

$$dt = \left(\frac{\rho.L}{K.\theta}\right)x\,dx$$

Total time taken by the layer of ice to increase in thickness by x

$$\int dt = \frac{\rho L}{K.\theta}\int x.dx$$

$$t = \frac{\rho L}{K.\theta}\frac{x^2}{2} + \text{constant}$$

When $t = 0,\ x = 0$

Hence the constant is zero.

$$\therefore \quad t = \frac{\rho L}{2K\theta}x^2 \quad \ldots(iv)$$

Example 8·5. *Find the time in which a layer of ice 3* cm *thick on the surface of a pond will increase its thickness by 1* mm *when the temperature of the surrounding air is* -20°C.

Thermal conductivity of ice = 0·005

Latent heat of ice = 80 cal/g

Density of ice at 0°C = 0·91 g/cm³ *(Calcutta 1966)*

$$\int dt = \frac{\rho L}{K\theta}\int x\,dx$$

$$t = \frac{\rho L}{2K\theta}\left[x_2^2 - x_1^2\right]$$

Here $\rho = 0{\cdot}91$ g/cm³

$L = 80$ cal/g

$K = 0{\cdot}005$

$\theta = 20$°C

$x_1 = 3$ cm

$x_2 = 3{\cdot}1$ cm

$$t = \frac{0{\cdot}91 \times 80}{2 \times 0{\cdot}005 \times 20}\left[(3{\cdot}1)^2 - (3)^2\right]$$

$= 222{\cdot}04$ s

$=$ **3 min 42 s approximately**

Example 8·6. *How much time will it take for a layer of ice of thickness 10* cm *to increase by 5* cm *on the surface of a pond when the temperature of the surroundings is* -10°C ?

$K = 0{\cdot}005$

$L = 80$ cal/g

$\rho = 0{\cdot}90$ g/cm³

Here $\int dt = \frac{\rho L}{K\theta}\int x\,dx$

$$t = \frac{\rho L}{2K\theta}(x_2^2 - x_1^2)$$

Here $x_1 = 10$ cm ; $x_2 = 15$ cm

$$t = \frac{0{\cdot}90 \times 80}{2 \times 0{\cdot}005 \times 10}\left[(15)^2 - (10)^2\right]$$

$= 9 \times 10^4$ s $=$ **25 hours**

8·17 Wiedemann-Franz Law

In 1853, Wiedemann and Franz, based on experimental results, put forward a law relating to the thermal conductivity and electrical conductivity of metals. According to this law :

The ratio of the thermal and electrical conductivities is the same for all metals at the same temperature. Moreover, the ratio is directly proportional to the absolute temperature of the metal.

Let K and σ be thermal and electrical conductivities of a metal at a temperature T degrees absolute,

$$\frac{K}{\sigma} \propto T$$

or

$$\frac{K}{\sigma T} = \text{constant for all metals}$$

This law holds good for a large number of metals between +100°C and −100°C. At low temperatures the ratio K/σ decreases and the value tends to be zero at absolute zero. As the temperature of the metal is decreased, the thermal and electrical conductivities of the metal increase. But the increase in the electrical conductivity is higher and its value tends to infinity at absolute zero.

This corresponds to the super-conducting state of the metal.

Drude explained that thermal and electrical conductivities are due to free electrons in metals. He derived the expression

$$\frac{K}{\sigma T} = \frac{3R^2}{JN^2e^2} = \text{constant},$$

where R is the universal gas constant, N is the number of molecules in one gram molecule, J is the Joule's mechanical equivalent of heat and e is the charge on the electron.

Values of $\frac{K}{\sigma T} \times 10^6$

Metal	*−100°C*	*−50°C*	*0°C*	*18°C*
Aluminium	1·81	1·98	2·09	2·13
Copper	2·17	2·26	2·30	2·32
Iron	2·98	2·93	2·97	2·99
Lead	2·54	2·52	2·53	2·51
Silver	2·29	2·36	2 33	2·33
Zinc	2·39	2·40	2 45	2·43

8·18 Practical Applications of Conduction of Heat

Metals are good conductors of heat and wood, felt, brick, glass, granite, cotton, wool, cork, ebonite, rubber are bad conductors of heat.

(1) Sauce pans, hot water buckets, kettles and other utensils are made of metal. They are provided with wooden or ebonite handles so that heat from the utensil is not conducted to the hand.

(2) Ice box has a double wall made of tin or iron. The space in between the two walls is packed with cork or felt. This is done because cork and felt are poor conductors of heat and prevent the flow of the outside heat into the box.

(3) Thick brick walls are used in the construction of a cold storage. Brick is a bad conductor of heat and does not allow outside heat to flow inside the cold storage.

(4) Woollen clothes have fine pores filled with air. Air and wool are bad conductors of heat. Heat from the body does not flow outside to the atmosphere. Therefore woollen clothes keep the body warm in winter.

(5) Two shirts keep the body warmer than a single shirt of the same material and double the thickness. Between the two shirts a fine layer of air acts as a bad conductor and does not allow the heat from the body to flow out to the surroundings.

(6) Quilts and bed clothings filled with cotton are used in winter. The air layers in the pores of the cotton are bad conductors of heat. Therefore the flow of heat to outside is prevented.

(7) A steel blade appears colder than a wooden handle in winter. Steel is a good conductor of heat. As soon as a person touches the blade, heat flows from the hand to the blade. Therefore it appears colder. Since wood is a bad conductor of heat, heat does not flow from the hand to the handle.

(8) In cold countries, the windows are provided with double doors. Air in between the two doors forms a non-conducting layer and does not allow heat to flow from inside to outside.

In hot countries also, double door windows are used. Heat does not flow from outside to inside because air forms a non-conducting layer in between the two doors.

(9) When a stopper fitted tightly to the bottle is to be removed the neck is gently heated. Glass is a poor conductor of heat. Neck expands but heat is not conducted to the stopper. The stopper can be removed easily.

8·19 Davy's Safety Lamp

It also is based on the principle of conduction of heat. A wire gauze is placed over a bunsen burner and the gas is lit above the wire gauze (Fig. 8·21). The gas comes out of the wire gauze. A flame appears at the top surface of the wire gauze. The gas below the wire gauze does not get sufficient heat for ignition. The wire gauze conducts away the heat of the flame above it and the temperature at the lower surface does not reach the ignition temperature.

In a Davy's safety lamp, the cylindrical metal gauze of high thermal conductivity surrounds the flame (Fig. 8·22). When this lamp is taken inside a mine, even if explosive gases are present, they do not get ignited because the wire gauze conducts away the heat of the flame. The temperature outside the wire gauze remains lower than the ignition temperature of the gases. In the absence of the wire gauze the gases outside can explode.

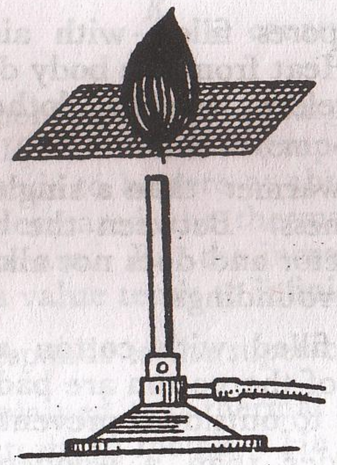


Fig. 8·21

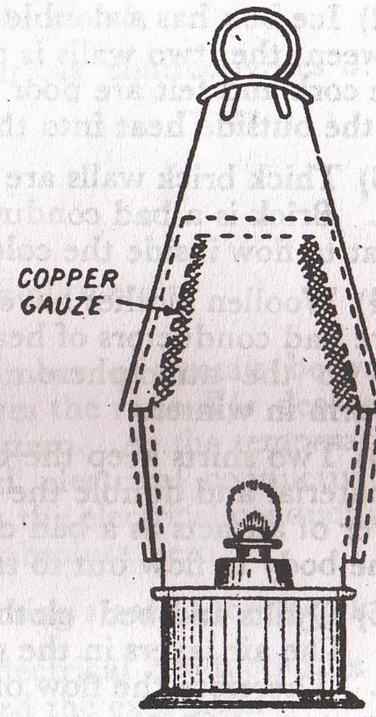


Fig. 8·22

As soon as a miner notices the presence of the explosive gases from the colour of the flame, he gives a warning signal. The work is stopped and the mine is thoroughly ventilated.

8·20 Convection

Experiment 1. Take a flask containing water. Add a large crystal of $KMnO_4$. Heat the flask (Fig. 8·23). Coloured streaks of

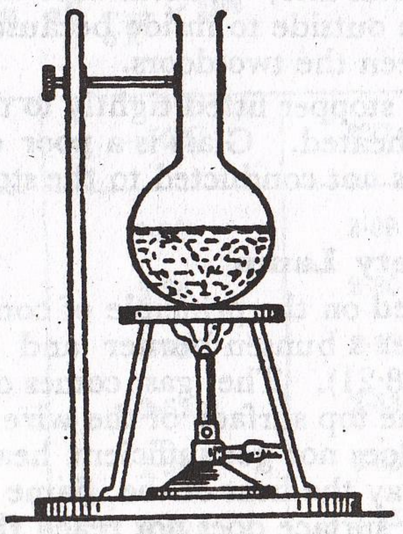


Fig. 8·23

water rise up and move to the sides. Water at the bottom gets heated and moves up. Water from the sides reaches the bottom, gets heated and rises up. The process continues. This phenomenon is called convection. Every molecule of water comes to the hot point, takes heat and moves up.

Experiment 2. Take a rectangular glass tube and fill it with water (Fig. 8·24) Pour a little charcoal powder in the tube. Heat the side tube gently. The convection currents are set up due to the movement of the heated water molecules. The direction of movement of water molecules is indicated by the movement of the charcoal particles.

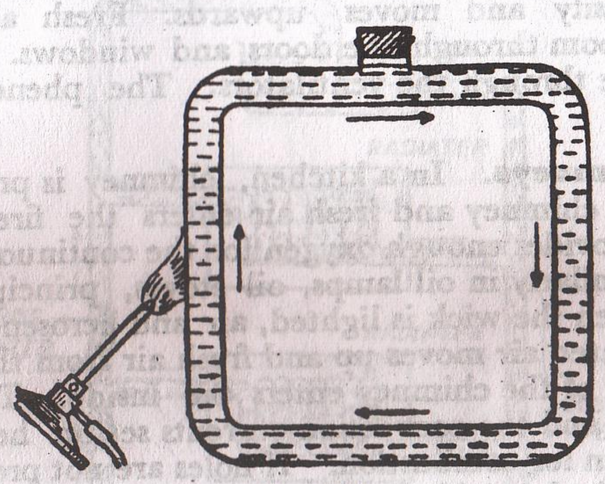


Fig. 8·24

Experiment 3. Take a candle and fix it at the bottom of a cylinder (Fig. 8·25). Light the candle. The flame becomes weaker and weaker and finally gets extinguished. Air in the cylinder gets heated and is pushed out. There is no fresh supply of air for the burning of the candle.

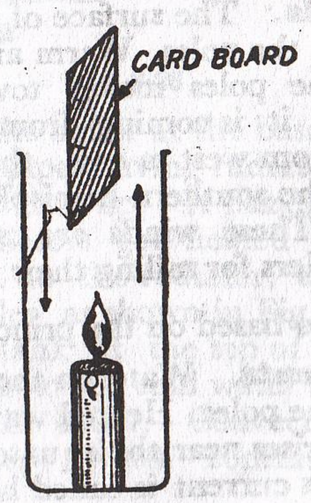


Fig. 8·25

Now, take a cardboard and hold it inside the cylinder. The space above the candle is divided into two parts. Light the candle. The candle continues to burn. Here air above the flame gets heated and moves up through one of the sides of the cardboard. Through

the other side of the cardboard fresh air moves in. Convection currents are set up and the candle continues to burn.

In mines, two chimneys are used. Underneath one of the chimneys fire is produced. Through the other chimney fresh air enters into the mines. Convection currents are produced. This provides proper ventilation in the mine.

8·21 Applications of Convection

(1) **Ventilation.** Rooms are provided with ventilators near the ceiling. Air in the room gets warmer due to respiration of people in the room. Warm air containing more of CO_2 and water vapour has less density and moves upwards. Fresh air from outside enters the room through the doors and windows. The impure air moves outside through the ventilators. The phenomenon is continuous.

(2) **Chimneys.** In a kitchen, chimney is provided. Hot air moves up the chimney and fresh air enters the fire place from outside. This provides enough oxygen for the continuous combustion of the fuel. Similarly in oil lamps, oil stoves, principle of a chimney is used. When the wick is lighted, air and kerosene oil burn above the wick. Heated air moves up and fresh air from the holes provided at the bottom of the chimney enters the inside. The phenomenon is continuous and the convection currents set up help in supplying enough oxygen for combustion. If holes are not provided, the flame gets extinguished quickly.

In a factory, a high chimney is provided. The rate of circulation of air depends on the difference in pressure between the two ends of the chimney. Higher the chimney, greater is the rate of circulation of air. Due to this reason, sufficient supply of oxygen is provided and the complete combustion of the fuel takes place.

(3) **Trade Winds.** The surface of the earth gets heated more at the equator than at the poles. Warm air at the equator moves up and cold air from the poles moves towards the equator. In the northern hemisphere, it is coming from the north and due to the rotation of the earth from west to east, the wind appears to come from north-east. In the southern hemisphere, the wind appears to be from south-west. These winds are called trade winds because they were used by traders for sailing their vessels in ancient days.

Monsoons are also based on the principle of convection.

(4) **Ocean Currents.** Water in the ocean at the equator gets heated more than at the poles. Heated water at the equator expands and the level of water rises near the equator. This hot water flows towards the poles. This current is called hot current or gulf streams. The cold water from the poles moves towards the equator beneath the ocean and this current is called the under current.

(5) **Land and Sea Breezes.** Near the sea, water becomes less warm than the land during day time. The heated air on the land surface moves up. Air from the surface of the sea moves towards the

sea shore. This is called sea breeze. Convection currents are set up During night when the land becomes cooler than water, the air over the surface of water is warmer and moves upward. Air from the land. moves towards the sea. This is called land breeze.

8·22 Central Heating System

In cold countries, the temperature in winter falls below 0°C. The rooms of a building are kept warm by a central heating system qased on the principle of convection.

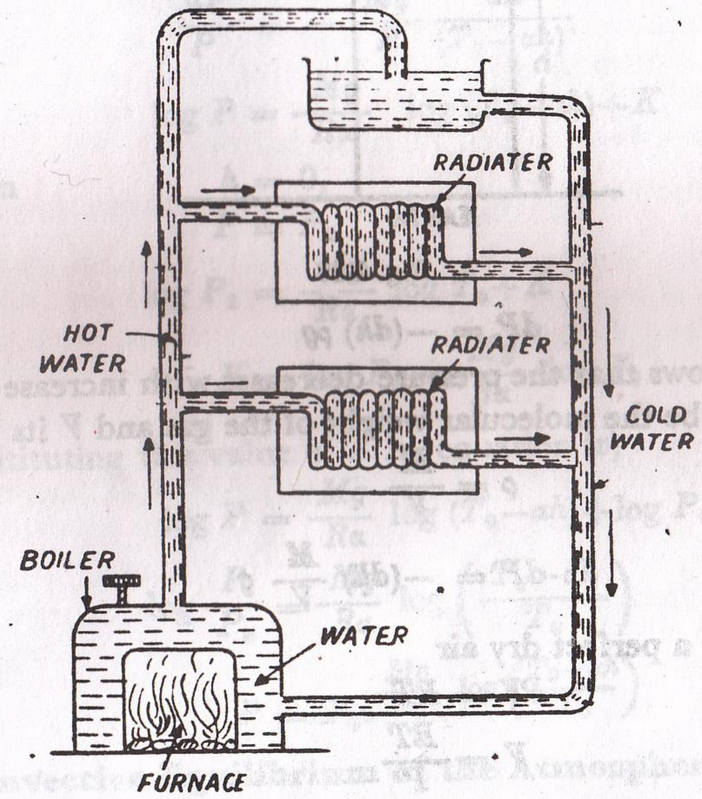


Fig. 8·26

Water is heated in the boiler at the basement of the building. The rooms are fitted with pipes having radiators fixed on the walls. Hot water from the boiler rises up. It passes through the radiators of different rooms. Radiators get heated and radiate heat to the room. After losing heat to the radiator, water becomes cold and returns back to the boiler as shown in Fig. 8·26. Hot water also reaches the cold water tank at the top of the building. The hot water flows from the boiler to the cold water tank and the cold water flows from the tank to the boiler. Convection currents are set up and the building is kept warm continuously at a constant temperature.

8·23 Change of Pressure with Height

The pressure of the atmosphere decreases with increase in height from sea level. The density of air is not the same at all levels. If the density of air were the same at all levels, the atmospheric pressure at sea level would correspond to a vertical column of 8 km of air only. But it has been found that air exists even at a height of 200 km.

Consider that the pressure of air at a height $h = P$. For an increase in height dh, the decrease in pressure is dP (Fig. 8·27).

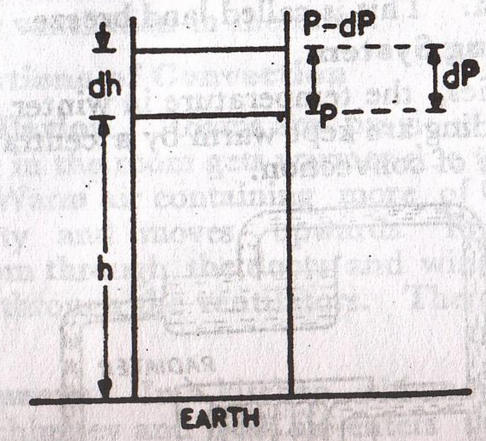


Fig. 8·27

$$dP = -(dh)\,\rho g \qquad \ldots(i)$$

[$-ve$ sign shows that the pressure decreases with increase in height]

Let M be the molecular weight of the gas and V its volume.

Then, $$\rho = \frac{M}{V}$$

and $$dP = -(dh)\,\frac{M}{V}\,g$$

But for a perfect dry air

$$PV = RT$$

or $$V = \frac{RT}{P}$$

$$\therefore \quad dP = -(dh)\,\frac{M \cdot Pg}{RT}$$

$$\frac{dP}{P} = -\frac{Mg}{RT}\,(dh) \qquad \ldots(ii)$$

Integrating

$$\log P = -\frac{Mg}{RT}\,h + C \quad \text{[where } C \text{ is a constant]}$$

When $h = 0$,

$P = P_0$

$$\therefore \quad C = \log P_0$$

and $$\log P = -\frac{Mg}{RT}\,h + \log P_0$$

$$\log_e \frac{P}{P_0} = -\frac{Mg}{RT}\,h \qquad \ldots(iii)$$

$$P = P_0 e^{-\frac{Mg}{RT}\,h} \qquad \ldots(iv)$$

Equation (ii) will be true only under isothermal conditions. But air temperature decreases uniformly with height. Assuming that the lapse rate is α in the lower portion of the atmosphere (troposphere),

$$T = T_0 - \alpha h$$

where T_0 is the temperature of the ground.

Substituting this value in equation (ii)

$$\therefore \quad \frac{dP}{P} = -\frac{Mg}{R}\,\frac{dh}{(T_0 - \alpha h)}$$

$$\log P = \frac{Mg}{R\alpha}\,\log (T_0 - \alpha h) + K \qquad \ldots(v)$$

When $h = 0$,

$P = P_0$

$$\therefore \quad \log P_0 = \frac{Mg}{R\alpha}\,\log T_0 + K$$

or $$K = \log P_0 - \frac{Mg}{R\alpha}\,\log T_0$$

Substituting this value of K in equation (v)

$$\log P = \frac{Mg}{R\alpha}\,\log (T_0 - \alpha h) + \log P_0 - \frac{Mg}{R\alpha}\log T_0$$

$$\log \frac{P}{P_0} = \frac{Mg}{R\alpha}\,\log\left(\frac{T_0 - \alpha h}{T_0}\right) \qquad \ldots(vi)$$

or $$P = P_0 e^{\frac{Mg}{R\alpha}\,\log\left(\frac{T_0 - \alpha h}{T_0}\right)} \qquad \ldots(vii)$$

8·24 Convective Equilibrium of the Atmosphere

The atmospheric temperature decreases with altitude upto a height of about 20 km. The rate of fall of temperature is about 5°C per km height and is known as the lapse rate. The atmosphere is divided into two regions.

(1) **Troposphere or the convective zone.** It is the region in which the temperature falls with increase in height from the ground.

(2) **Stratosphere or advective zone.** It is the region in which the decrease in temperature does not take place with increase in height.

The layer that separates these two regions is known as *tropopause*. The height of tropopause is different at different places on the earth. It is about 14 km at the equator and about 10 km at the poles.

The fall in temperature with altitude in the troposphere is due to convection. When the heat radiations from the sun fall on the surface of the earth, it gets heated. The atmospheric air surrounding the earth gets heated by conduction and radiation. The heated air

moves up and convection currents are set up. The heated air that moves up from the regions of higher to lower pressure is adiabatically cooled. Similarly when the colder air moves down from lower to higher pressure regions it is adiabatically heated. Thus a *convective equilibrium is set up* and there is a gradual fall of temperature with increase in height.

The earth gets heated up due to the heat radiations from the sun. The layers of the atmosphere close to the ground get heated up and convection currents start in the atmosphere. As the warm air rises up into the region of low pressure, it **expands adiabatically.** For an atmosphere, in convective equilibrium, there is a vertical fall of temperature from the earth's surface. The **dry adiabatic lapse rate** is calculated as follows :

The relation between pressure and temperature for an adiabatic process is

$$\frac{P^{\gamma-1}}{T^{\gamma}} = \text{const.}$$

or $$P^{\gamma-1}\,T^{-\gamma} = \text{const.}$$

Differentiating

$$(\gamma-1)\,P^{\gamma-2}\,dP.T^{-\gamma}+P^{\gamma-1}(-\gamma)\,T^{-\gamma-1}\,dT = 0$$

Dividing by $P^{\gamma-1}\,T^{-\gamma}$

$$(\gamma-1)\frac{dP}{P}+(-\gamma)\frac{dT}{T} = 0$$

$$\frac{dP}{P} = \frac{\gamma}{\gamma-1}\frac{dT}{T} \qquad \ldots(i)$$

For an increase in height dh, the decrease in pressure is dP

$\therefore$ $$dP = -\rho g\,dh = -\frac{M}{V}\,g\,dh$$

But $$PV = RT$$

or $$V = \frac{RT}{P}$$

$\therefore$ $$dP = -\frac{MP}{RT}\,g\,dh$$

or $$\frac{dP}{P} = -\frac{Mg}{RT}\,dh \qquad \ldots(ii)$$

Equating (i) and (ii)

$$\left(\frac{\gamma}{\gamma-1}\right)\frac{dT}{T} = -\frac{Mg}{RT}\,dh$$

$$\frac{dT}{dh} = -\frac{Mg}{R}\left(\frac{\gamma-1}{\gamma}\right) \qquad \ldots(iii)$$

This equation holds good only for perfect dry air. The lapse rate $\frac{dT}{dh}$ can be calculated from equation (iii).

Substituting the values,

$M = 29$ g

$g = 981$ cm/s^2

$R = 8{\cdot}31 \times 10^7$ ergs per gram mol per K,

and $\gamma = 1{\cdot}4$

$$\frac{dT}{dh} = -\frac{29\times981}{8{\cdot}31\times10^7}\left(\frac{1{\cdot}40-1}{1{\cdot}40}\right)$$

$= 10^{-4}$ K per cm

$= 10^{-4}$ °C per cm

Thus, the lapse rate for a height of 1 km $= 10^{-4}\times10^5 = 10$°C. But it has been found that the average lapse rate is lower than this value. Under average conditions the lapse rate has been found to be between 5°C and 6·5°C per km.

However at night, when the earth is radiating heat to the atmosphere, the layers of air nearer the surface may cool to a temperature lower than that of the upper layers. Then a *negative lapse rate is set up.*

8·25 Differential Air Thermoscope

A differential air thermoscope consists of two glass bulbs *A* and *B* connected by a narrow glass tubing. The U-tube contains

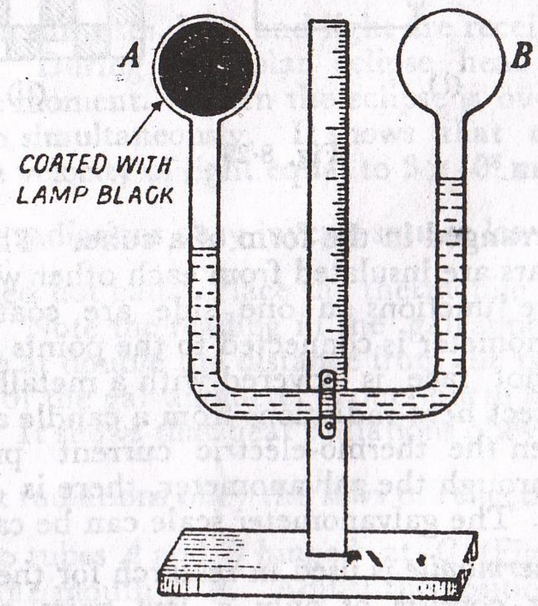


Fig. 8·28

sulphuric acid. The bulbs *A* and *B* contain air and when they are at the same temperature, there is no difference in level of the liquid in the two limbs. The bulb *A* is coated with lamp black so that it can completely absorb the whole of the heat radiations falling on it (Fig. 8·28).

When A is exposed to heat radiations, it absorbs heat energy. Air inside the bulb A expands and there is difference in level of the liquid in the two limbs. This thermoscope is very sensitive and can detect heat radiations of even feeble intensity (*i.e.*, from a candle at a large distance).

8·26 Thermopile

The thermopile originally designed by *Melloni* consisted of a number of thermocouples joined in series. The thermocouples are made of bismuth and antimony. The junctions on one side are coated with lamp black and are exposed to heat radiations The junctions on the other side are kept cold. The two ends of the thermopile are connected to a sensitive galvanometer (Fig. 8·29).

The deflection in the galvanometer measures the intensity of heat radiations and the scale can be calibrated.

The improved form of a thermopile, which is commonly used, consists of a large number of thermopiles. The bars of antimony

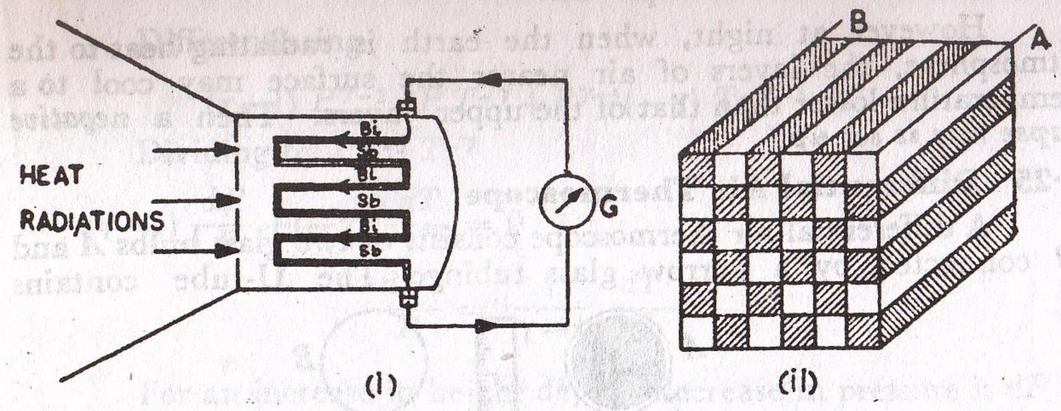


Fig. 8·29

and bismuth are arranged in the form of a cube. The junctions are soldered but the bars are insulated from each other with mica strips (Fig. 8·29). All the junctions on one side are coated with lamp-black. The galvanometer is connected to the points A and B. When not in use, the hot face is covered with a metallic cup. Such a thermopile can detect heat radiations from a candle at a distance of 100 metres. When the thermo-electric current produced in the thermopile flows through the galvanometer, there is a deflection in the galvanometer. The galvanometer scale can be calibrated.

The *linear thermopile* is used in research for the study of *infra-red* radiations. It consists of only a few pairs of thermocouples connected to a sensitive galvanometer. The hot junctions are arranged in a line.

The thermopiles can be made sensitive by mounting the thermopile in vacuum and using very short connecting wires. The chief drawback of a termopile consists in the comparative slowness of its indication and also the long time it takes to return to its zero reading.

8·27 Properties of Thermal Radiations

Heat radiations have properties similar to light radiations. They are electromagnetic waves of longer wavelength. The range

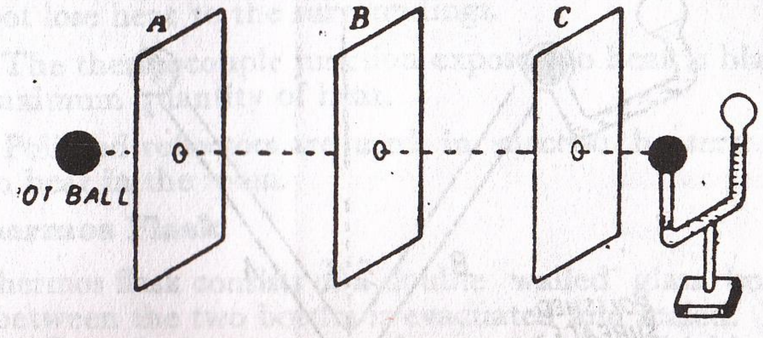


Fig. 8·30

of wavelengths of heat radiations is from 3 cm to 8×10^{-5} cm.

(1) Heat radiations travel in straight lines.

Take three similar cardboards having holes at the same height. Place a red hot ball in front of the hole of the first cardboard. Bring the blackened bulb of the differential air thermoscope near the hole of the third cardboard (Fig. 8·30). When the hot ball, the three holes and the bulb of the thermoscope are in the same straight line, maximum difference in level is noted. When one of the cardboards is displaced, the thermoscope is not affected. This shows that heat radiations travel in straight lines.

(2) Heat radiations travel with the velocity of light.

When the sun rises, heat and light are received simultaneously on the earth. During the solar eclipse heat and light are cut off at the same moment. When the eclipse is over, heat and light reach the earth simultaneously. It shows that the heat radiations travel with the velocity of light equal to 3×10^8 m/s.

(3) Heat radiations obey inverse square law.

Take a red hot ball. Place the thermopile at a fixed distance from the ball. Note the reading in the galvanometer. Now, place the thermopile at double the distance from the ball. It is found that the deflection of the galvanometer is one-fourth of the deflection in the first case. It shows that heat radiations obey inverse square law.

(4) Heat radiations obey the laws of reflection.

Take two tubes A and B hinged at C (Fig. 8·31). Keep the metal ball at the mouth of A. Adjust the position of B to get the maximum difference in level in the thermoscope. It is found that the difference in level is maximum when the two tubes are equally inclined to the normal at C. It means $\angle i = \angle r$.

Take a concave metallic reflecting surface. Direct it towards the sun. A small piece of paper placed at the focus of the mirror catches fire. All the heat radiations incident on the mirror after

reflection converge at its focus (Fig. 8·32). Room heaters are provided with concave or elliptical reflectors. The heater element is kept at the focus of the mirrors.

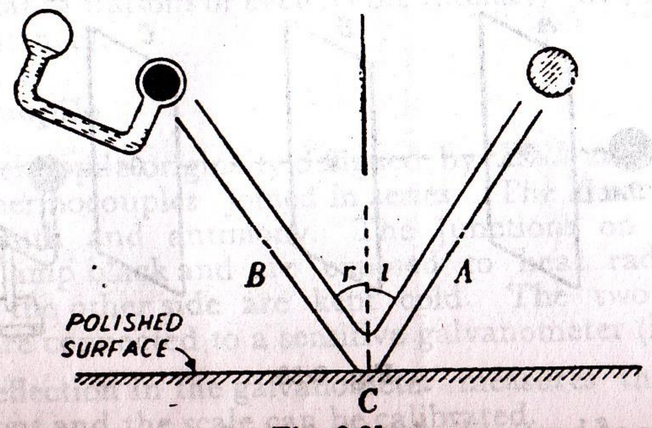


Fig. 8·31

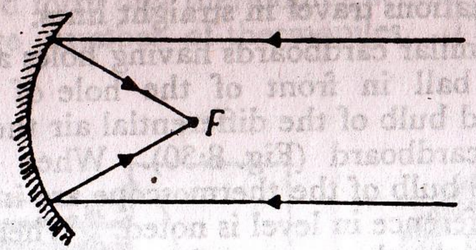


Fig. 8·32

(5) Heat radiations obey the laws of refraction.

Take a convex lens and keep a small paper at its focus. When the lens is directed towards the sun's rays, the paper catches fire. The parallel heat radiations from the sun after refraction from the lens converge at its focus.

(6) Heat radiations get diffused when they are incident on a rough and unpolished surface.

(7) Heat radiations can travel through vacuum.

(8) Heat radiations do not affect the medium through which they pass. When sun's rays are allowed to pass through a convex lens, they converge at the focus of the lens. The lens does not get heated but a paper at the focus catches fire.

8·28 Applications of Heat Radiations

(1) White clothes are preferred in summer and dark coloured clothes in winter.

When heat radiations fall on white clothes, they are reflected back. No heat is absorbed by the clothes and a person does not get heat from outside in summer. Dark clothes in winter will absorb the heat radiations falling on them and keep the body warm.

(2) Cooking utensils are blackened at the bottom and polished on the upper surface. Black surface will absorb the whole of the heat from the furnace and the upper surface will not allow the heat inside the utensil to flow out.

(3) Hot water pipes and radiators used in rooms are painted black so that they can radiate maximum amount of heat to the room. The same pipes outside the rooms are painted white so that they do not lose heat to the surroundings.

(4) The thermocouple junction exposed to heat is blackened to absorb maximum quantity of heat.

(5) Polished reflectors are used in electric heaters to reflect maximum heat in the room.

8·29 Thermos Flask

A thermos flask consists of a double walled glass bottle. The space in between the two bottles is evacuated and scaled. The inner surface of *B* and the outer surface of *A* are highly polished (*i.e.* silvered) (Fig. 8·33).

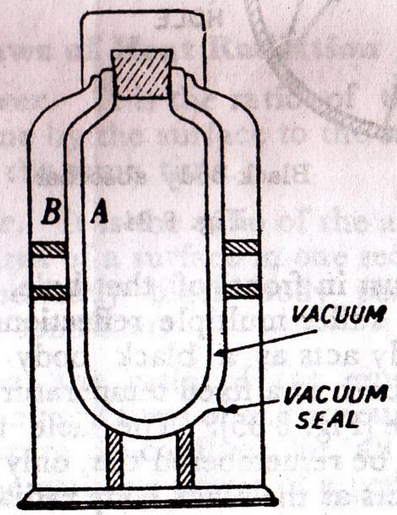


Fig. 8·33

When a hot liquid is kept in the bottle, it remains hot for a long time. The outer polished surface of *A* does not radiate heat. Even if a little quantity of heat is radiated by *A*, most of it is reflected back by the polished surface of *B*.

The evacuation of the space in between *A* and *B* helps in the elimination of the loss of heat by conduction and convection.

Similarly ice kept inside the flask will not melt for a long time because heat radiations from outside cannot enter the inside of the bottle.

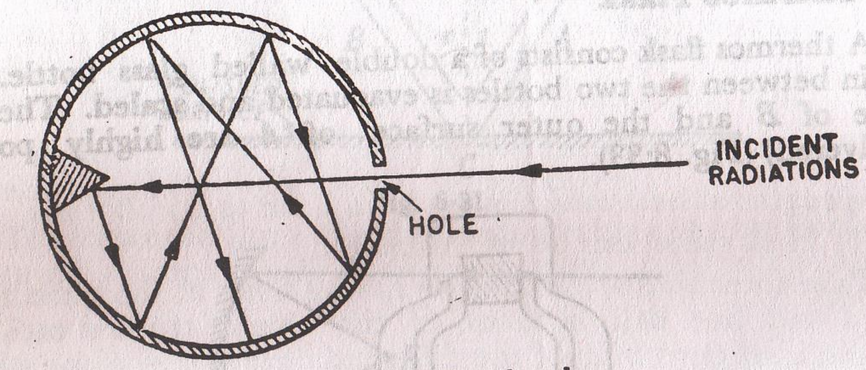
8·30 Black Body

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** radiations. 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.

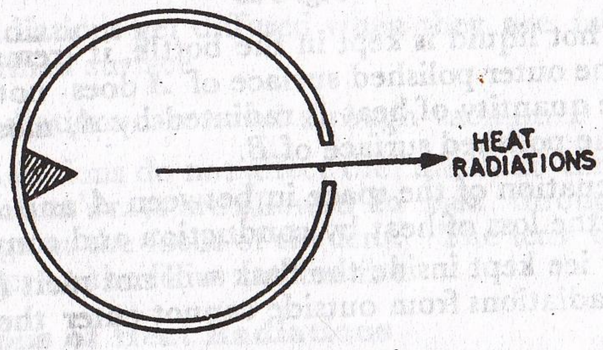
A hollow copper sphere is taken and is coated with lamp black on its inner surface [Fig. 8 34]. A fine hole is made and a pointed



Black body absorber

Fig. 8·34

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 a bath at a fixed temperature, the heat radiations come out of the hole [Fig. 8·35]. 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.



Black body emitter

Fig. 8·35

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. 8·36). The temperature is measured with the help of a thermocouple arrangement. Heat radiations emerge out of the hole.

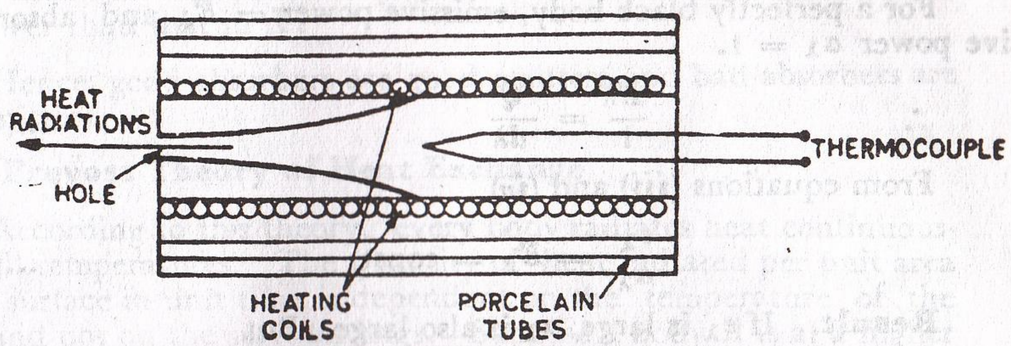


Fig. 8·36

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.

8·31 Kirchhoff's Laws of Heat Radiation

Absorptive power. It is the ratio of the amount of heat absorbed in a given time by the surface to the amount of heat incident on the surface in the same time.

Emissive power. It is the ratio of the amount of heat radiations emitted by unit area of a surface in one second to the amount of heat radiated by a perfectly black body per unit area in one second under identical conditions.

The law states that the ratio of the emissive power to the absorptive power for the radiations of a particular wavelength and at a particular temperature is constant for all bodies. Moreover, this ratio is equal to the emissive power of a perfectly black body.

Suppose e_λ and a_λ are the emissive and absorptive powers of a body. Let Q be the quantity of heat radiations incident on the surface in one second, Q_1 is the quantity of heat adsorbed by the surface and Q_2 is the quantity of heat reflected by it.

As the body radiates heat, at all temperatures, the heat emitted by it in one second $= e_\lambda d\lambda$

Total heat falling on the surface $= Q$ ...(i)

Total heat given out by the surface

$$= (Q - Q_1) + e_\lambda d\lambda \quad \text{...(ii)}$$

For equilibrium, (i) and (ii) are equal

$$\therefore \quad (Q - Q_1) + e_\lambda d\lambda = Q$$

But $$a_\lambda = \frac{Q_1}{Q}$$

$$Q_1 = a_\lambda Q$$

$$Q - a_\lambda Q + e_\lambda d\lambda = Q$$

or $$\frac{e_\lambda}{a_\lambda} = \frac{Q}{d\lambda} = \text{const.} \quad \ldots(iii)$$

For a perfectly black body, emissive power $= E_\lambda$ and absorptive power $a_\lambda = 1$.

$$\therefore \quad \frac{E\lambda}{1} = \frac{Q}{d\lambda} \quad \ldots(iv)$$

From equations (*iii*) and (*iv*)

$$\frac{e_\lambda}{a_\lambda} = E_\lambda = \text{const.} \quad \ldots(v)$$

Result. If e_λ is large, a_λ is also large. But

$$r_\lambda = \frac{Q - Q_1}{Q}$$

$$= 1 - a_\lambda$$

Therefore r_λ is small. Here r_λ is the reflecting power of the surface. It means good emitters are good absorbers but bad reflectors. Dull black surfaces are good emitters and good absorbers but bad reflectors.

(1) If e_λ is small, a_λ is also small and r_λ is large. It means bad emitters are bad absorbers but good reflectors. Highly polished surfaces are bad emitters and bad absorbers but good reflectors.

These results are verified by Ritchie's experiment.

Ritchie's Experiment. It consists of two cylindrical vessels A and B connected to the glass tubing XY (Fig. 8·37). One set of faces of A and B is blackened while the other set of faces is polished.

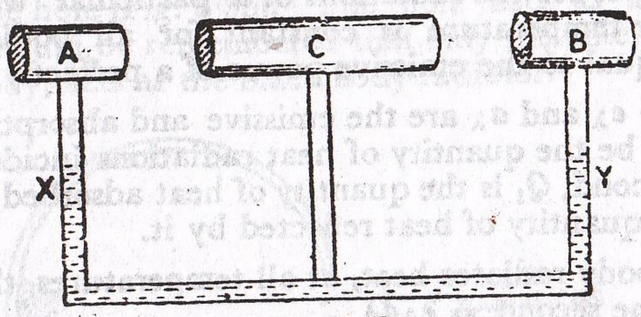


Fig. 8·37

C is another cylindrical vessel containing hot water and fixed on a stand between A and B so that the three cylinders are co-axial. One face of C is blackened while the other is polished. XY serves as a differential air thermoscope.

Initially, the blackened face of C is towards the polished face of A and the polished face of C is towards the blackened face of B. The level of the liquid in the limbs X and Y will be the same. Now, turn C so that the polished face of C is towards the polished face of A. The quantity of heat emitted by the polished face of C is very small. Also the quantity of heat absorbed by the polished face of A is small. Therefore the rise in temperature of air inside A is very small. On the other hand the quantity of heat emitted by the blackened face of

C is large and also the quantity of heat absorbed by the blackened face of B is large. Therefore, rise in temperature of air inside B is higher than that in A. Consequently the level of liquid in the limb Y is lower than that in X.

Hence, good absorbers are good emitters and bad absorbers are bad emitters.

8·32 Prevost Theory of Heat Exchange

According to this theory, every body radiates heat continuously at all temperatures. The quantity of heat radiated per unit area of the surface in unit time is dependent on the temperature of the body and not on the surroundings. Suppose a body A is at a higher temperature than the surroundings. It will radiate more quantity of heat to the surroundings and it will absorb less heat from the surroundings. Consequently the temperature of the body falls. When the temperature of the body becomes equal to that of the surroundings, it is in thermal equilibrium with the surroundings. The amount of heat radiated is equal to the amount of heat absorbed by it. Similarly, when a body is at a temperature lower than that of the surroundings, it will radiate less heat and absorb more heat.

Thus, all bodies at all temperatures are in a state of dynamic thermal equilibrium when they are at the same temperature. Moreover, the amount of heat radiated from a body decreases with the fall in temperature of the body. When the body is at the absolute zero temperature (−273°C), it will not radiate any heat energy because the kinetic energy of the molecules is zero at the absolute zero temperature.

8·33 Lummer and Kurlbaum Bolometer

It is used to measure the intensity of heat radiations. It consists of four similar grids made of platinum. The grids 1 and 4 are

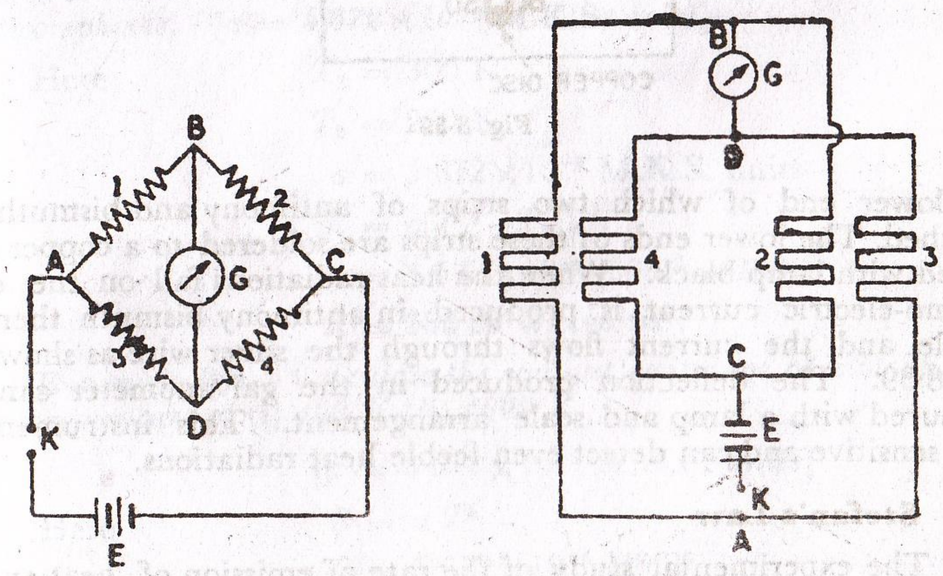


Fig. 8·38

coated with platinum black and are exposed to the heat radiations. The grids 2 and 3 are shielded.

The grids are connected in the four arms of a Wheatstone's bridge as shown in Fig. 8·38. Initially the balance point is adjusted. When the heat radiations fall on 1 and 4, their electrical resistance increases and the balance point is disturbed. The deflection in the galvanometer is observed. The scale of the galvanometer can be initially calibrated with heat radiations of known intensity. This bolometer is very sensitive and can detect very small changes of temperature of the order of 10^{-4} °C.

8·34 Boy's Radiomicrometer

It is a combination of a moving coil galvanometer and a thermocouple. It consists of a single loop of silver or copper wire A, to

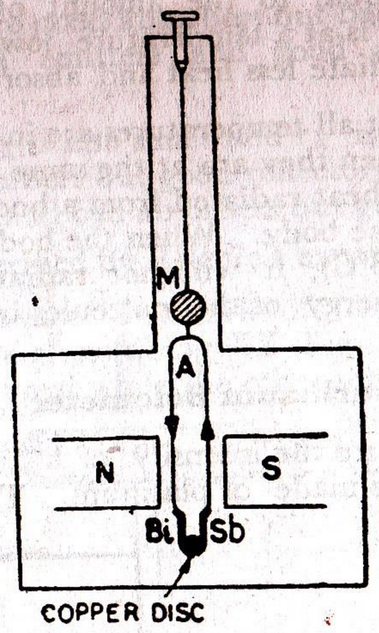


Fig. 8·39

the lower end of which two strips of antimony and bismuth are attached. The lower ends of these strips are soldered to a copper disc coated with lamp black. When the heat radiations fall on the disc, thermo-electric current is produced in antimony-bismuth thermocouple and the current flows through the silver wire as shown in Fig. 8·39. The deflection produced in the galvanometer can be measured with a lamp and scale arrangement. This instrument is very sensitive and can detect even feeble heat radiations.

8·35 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 the fourth power of its absolute temperature*

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

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

$$R = e\,\sigma\,T^4 \qquad \ldots(ii)$$

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 upto 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,

$$R \propto (T_1^4 - T_2^4)$$
$$R = \sigma\,(T_1^4 - T_2^4) \qquad \ldots(iii)$$

If the body has an emissitivity e,

then
$$R = e\sigma\,(T_1^4 - T_2^4) \qquad \ldots(iv)$$

Example 8·7. *Two large closely spaced concentric spheres (both are black body radiators) are maintained at temperatures of 200 K and 300 K respectively. The space in between the two spheres is evacuated. Calculate the net rate of energy transfer between the two spheres.* [$\sigma = 5.672 \times 10^{-8}$ M.K.S. units]

Here
$$T_1 = 300 \text{ K}$$
$$T_2 = 200 \text{ K}$$
$$\sigma = 5{\cdot}672 \times 10^{-8} \text{ M.K.S. units}$$
$$R = \sigma[T_1^4 - T_2^4]$$
$$= 5{\cdot}672 \times 10^{-8}[(300)^4 - (200)^4]$$
$$R = \mathbf{368{\cdot}68 \text{ watts/m}^2}$$

Example 8·8. *Calculate the radiant emittance of a black body at a temperature of (i) 400 K (ii) 4000 K.*

[$\sigma = 5{\cdot}672 \times 10^{-8}$ *M.K.S. units*]

Here
$$R = \sigma T^4$$

(*i*)
$$R = 5{\cdot}672 \times 10^{-8}\,[400]^4$$
$$= \mathbf{1452 \text{ watts/m}^2}$$

(*ii*)
$$R = 5{\cdot}672 \times 10^{-8}[4000]^4 = 1452 \times 10^4 \text{ watts/m}^2$$
$$= \mathbf{14520 \text{ kilo-watts/m}^2}$$

Example 8·9. *The relative emittance of tungsten is approximately 0·35. A tungsten sphere of surface area 10^{-3} sq metres is suspended inside a large evacuated enclosure whose walls are at 300 K. What power input is required to maintain the sphere at a temperature of 3000 K? The conduction of heat along the supports can be neglected.* [$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units]

$$R = \sigma A e[T^4 - T_0^4]$$

Here $A = 10^{-3}$ sq metres

$e = 0{\cdot}35$

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units

$$R = 5{\cdot}672 \times 10^{-8} \times 10^{-3} \times 0{\cdot}35[(3000)^4 - (300)^4]$$

$$= \mathbf{1609 \text{ watts}}$$

The power input $= \mathbf{1609 \text{ watts.}}$

Example 8·10. *An aluminium foil of relative emittance 0·1 is placed in between two concentric spheres at temperatures 300 K and 200 K respectively. Calculate the temperature of the foil after the steady state is reached. Assume that the spheres are perfect black body radiators. Also calculate the rate of energy transfer between one of the spheres and the foil.* [$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units.)

Here $T_1 = 300$ K

$T_2 = 200$ K

$e = 0{\cdot}1$

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units.

(*i*) Let x be the temperature of the foil. After the steady state is reached,

$$e\sigma(T_1^4 - x^4) = e\sigma(x^4 - T_2^4)$$

or $$[(300)^4 - x^4] = [x^4 - 200)^4]$$

$$x^4 = 48{\cdot}5 \times 10^8$$

$$\mathbf{x = 263{\cdot}8 \text{ K}}$$

(*ii*) $$R = e\sigma(T_1^4 - x^4)$$

$$R = 0{\cdot}1 \times 5{\cdot}672 \times 10^{-8}[(300)^4 - (263{\cdot}8)^4]$$

$$\mathbf{R = 18{\cdot}5 \text{ watts/m}^2}$$

Example 8·11. *Calculate the energy radiated per minute from the filament of an incandescent lamp at 2000 K, if the surface area is $5{\cdot}0 \times 10^{-5}$ sq metres and its relative emittance is 0·85.*

$$E = Ae\sigma t\,(T^4)$$

$A = 5 \times 10^{-5}$ m^2

$e = 0{\cdot}85$

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units

$t = 60$ s

$T = 2000$ K

$$E = 5 \times 10^{-5} \times 0{\cdot}85 \times 5{\cdot}672 \times 10^{-8} \times 60 \times (2000)^4$$

$$E = \mathbf{2315 \text{ joules}}$$

Example 8·12 *An iron furnace radiates $1{\cdot}53 \times 10^5$ calories per hour through an opening of cross section 10^{-4} sq metre. If the relative emittance of the furnace is 0·80, calculate the temperature of the furnace. Given* $\sigma = 1{\cdot}36 \times 10^{-8}$ cal/m^2-s-K^4

$$E = Ae\,\sigma\, t(T^4)$$

$$E = 1{\cdot}53 \times 10^5 \text{ calories}$$

$$A = 10^{-4} \text{ m}^2$$

$$e = 0{\cdot}80$$

$$t = 3600 \text{ s}$$

$$T = ?$$

$$T^4 = \frac{E}{Ae\,\sigma t}$$

$$T = \left(\frac{E}{Ae\,\sigma t}\right)^{\frac{1}{4}}$$

$$= \left[\frac{1{\cdot}53 \times 10^5}{10^{-4} \times 0{\cdot}80 \times 1{\cdot}36 \times 10^{-8} \times 3600}\right]^{\frac{1}{4}}$$

$$T = \mathbf{2500 \text{ K}}$$

8·36 Mathematical Derivation of Stefan's Law

The fact that black body radiations exert pressure similar to a gas, helps in applying thermodynamics to heat radiations.

Let ψ be the energy density of radiations inside a uniform temperature enclosure at temperature T. P is the pressure and V is the volume.

Applying the first law of thermodynamics

$$\delta H = dU + P.dV \qquad \ldots(i)$$

Applying thermodynamical relation

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \qquad \ldots(ii)$$

$$\left(\frac{\partial U + P\partial V}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v$$

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P \qquad \ldots(iii)$$

Now $U = V\psi$

and $$P = \frac{\psi}{3}$$

or $$\left[\frac{\partial U}{\partial V}\right]_T = \psi$$

Here ψ is a function of temperature alone.

Substituting these values in equation (*iii*),

$$\psi = \frac{T}{3}\frac{d\psi}{dT} - \frac{\psi}{3}$$

$$\frac{4\psi}{3} = \frac{T}{3}\frac{d\psi}{dT}$$

or $$\frac{d\psi}{\psi} = 4\frac{dT}{T}$$

Integrating, $\log \psi = 4 \log T + \text{constant}$ ...(*iv*)

or $$\psi = KT^4$$

Here K is a constant

Also the total rate of emission per unit area of a black body is proportional to the energy density.

$$\therefore \quad R \propto \psi \propto T^4 \qquad \ldots(v)$$

$$\therefore \quad R = \sigma T^4$$

where σ is Stefan's constant.

The value of Stefan's constant in C.G.S. system is $5{\cdot}672 \times 10^{-5}$ C.G.S. units and in M.K.S. system it is $5{\cdot}672 \times 10^{-8}$ M.K.S. units.

8·37 Derivation of Newton's Law of Cooling from Stefan's Law

Stefan's law is applicable for all temperatures of a hot body. But Newton's Law is applicable when the difference of temperature between the hot body and the surrounding is small. Consider a hot body at a temperature T_1 placed in a uniform temperature enclosure at T_2. According to Stefan's law,

$$R = e\sigma(T_1^4 - T_2^4) \qquad \ldots(i)$$

Here e is the emissitivity of the surface of the hot body

$$R = e\sigma(T_1 - T_2)(T_1^3 + T_1^2T_2 + T_1T_2^2 + T_2^3)$$

As $(T_1 - T_2)$ is small, T_1 can be taken approximately equal to T_2.

Then, $$R = e\sigma(T_1 - T_2)(T_2^3 + T_2^3 + T_2^3 + T_2^3)$$

$$R = 4e\sigma T_2^3(T_1 - T_2)$$

Taking $4e\sigma T_2^3 = k$

$$R = k(T_1 - T_2) \qquad \ldots(ii)$$

or $$R \propto (T_1 - T_2)$$

This equation represents Newton's law of cooling and is true when the difference of temperature is small.

8·38 Experimental Verification of Stefan's Law

In 1897, Lummer and Pringsheim experimentally verified Stefan's law over a wide range of temperature (100°C to 1,300°C).

The apparatus consisted of a black body C. For temperatures between 200°C and 600°C, a hollow copper sphere coated inside with

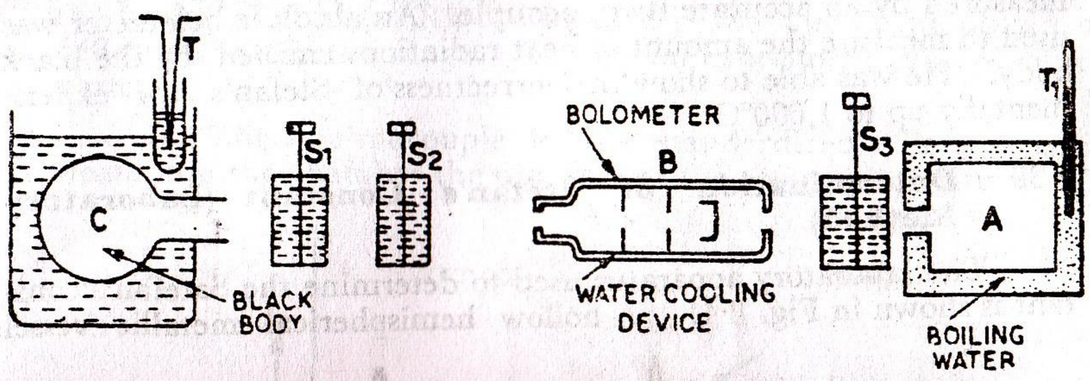


Fig. 8·40

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 1,300°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. 8·40).

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.

The 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 $$\theta \propto R$$

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

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.

8·39 Determination of Stefan's Constant (Laboratory Method)

The laboratory apparatus used to determine the Satefan's constant is shown in Fig. 8·41. A hollow hemispherical metallic vessel

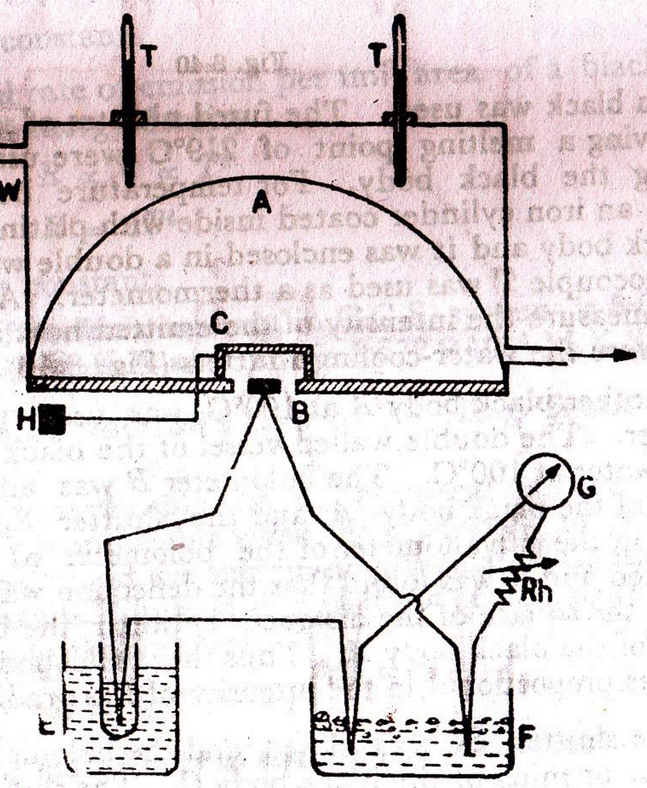


Fig. 8·41

A is enclosed in a wooden box W. The inner surface of A is coated with lamp black and the wooden box W is lined with tin plates. The whole apparatus is placed on a wooden base having a small hole at its centre. The vessel A is heated by passing steam inside the box and A acts as a black body radiator. The thermometers T T record the temperature of A.

A small silver disc B whose upper surface is coated with lamp black is placed at the central hole. The ebonite covering C is used to cover and uncover the disc B from the radiations of the enclosure. It can be arranged from outside with the help of the handle H. The disc B is connected to a thermocouple arrangement. One junction

of the thermocouple is immersed in a tube containing oil. The tube is surrounded by a beaker containing water. A sensitive galvanometer G is used in the circuit. The leads connected to the terminals of the galvanometer are immersed in cotton wool in the box F to avoid any distribution effect due to the difference of temperature in the leads. A rheostat Rh can be used in the circuit to obtain the deflection within the range. The actual experiment consists of two parts.

1. The thermocouple is first standardized. Before passing steam into the chamber the disc B is at the room temperature. The

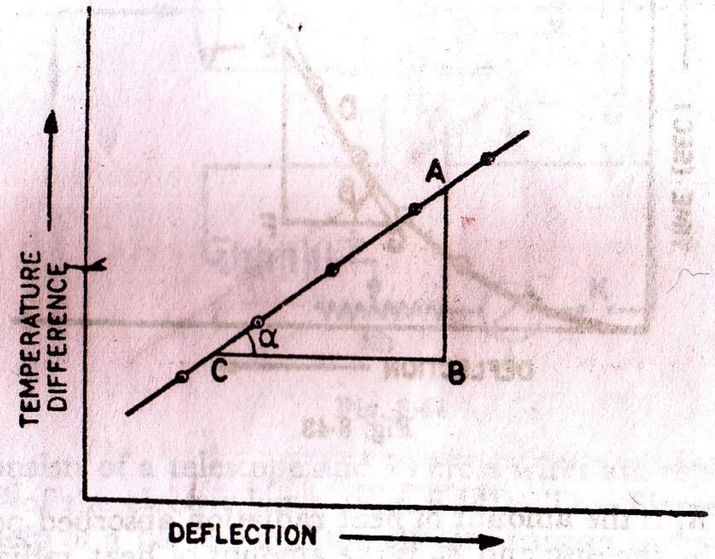


Fig. 8·42

water bath E acts as a hot junction. It is heated and at various temperatures of the hot junction, the corresponding deflections in the galvanometer are noted. A graph between the difference of temperature of the hot junction and the room temperature along the Y-axis and galvanometer deflection along X-axis is plotted (Fig. 8·42). From the graph,

$$\frac{dT}{d\theta} = \tan \alpha = \frac{AB}{BC} \qquad \ldots(i)$$

2. The disc is completely covered with C and steam is passed into the chamber. After some time, the thermometers T T show constant temperature. The bath E is kept at room temperature. With the help of the handle H, the cover C is tilted so that the upper surface of the disc B receives the radiations from the enclosure. The deflections in the galvanometer are observed after equal intervals of time (say 10 seconds). A graph is plotted between time and deflection (Fig. 8·43). A tangent is drawn on the curve at a point D.

$$\frac{dt}{d\theta} = \tan \beta = \frac{EF}{GF} \qquad \ldots(ii)$$

Theory

Let, at any instant, the temperature of the enclosure and the disc be T_1 and T_2 (degrees Kelvin) respectively. The disc will absorb

more heat from the surroundings and radiate less heat to the surroundings. Its temperature will rise. From Stefan's law,

$$R_1 = \sigma T_1^4 \text{ and } R_2 = \sigma T_2^4$$

$$\therefore \quad (R_1 - R_2) = \sigma(T_1^4 - T_2^4) \qquad \ldots(iii)$$

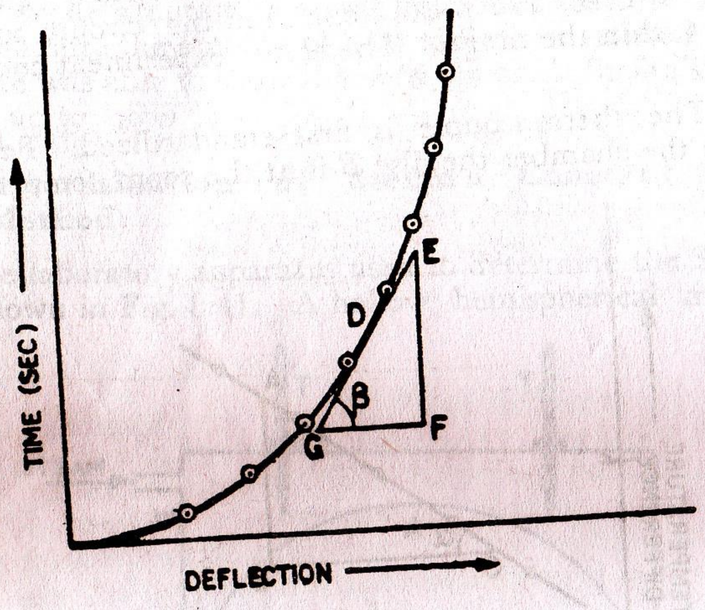


Fig. 8·43

Here R_1 is the amount of heat radiation absorbed per unit area per second by the disc and R_2 is the amount of heat radiation emitted per unit area per second by the disc.

Let the mass of the disc be m, specific heat S, rate of rise of temperature dT/dt, and area of the upper surface A.

Then $$\frac{(R_1 - R_2)\,A}{J} = mS\frac{dT}{dt}$$

$$\frac{\sigma(T_1^4 - T_2^4)A}{J} = mS\frac{dT}{dt}$$

$$\sigma = \frac{JmS}{A(T_1^4 - T_2^4)} \times \frac{dT}{dt} \qquad \ldots(iv)$$

To find $\frac{dT}{dt}$, equations (i) and (ii) are used.

$$\frac{dT}{dt} = \frac{dT}{d\theta} \times \frac{d\theta}{dt} = \frac{\tan\alpha}{\tan\beta}$$

To find T_2, the deflection in the galvanometer corresponding to the point D on graph in Fig. 8·43 is noted and for this deflection the temperature difference from the graph (Fig. 8·42) is noted. To this reading add the room temperature and find T_2 in degrees Kelvin.

Substituting these values in equation (iv)

$$\sigma = \frac{JmS\tan\alpha}{A(T_1^4 - T_2^4)\tan\beta} \qquad \ldots(v)$$

Hence σ can be calculated.

8·40 Disappearing Filament Optical Pyrometer

The instrument was designed by Holborn, Kurlbaum and Henning.

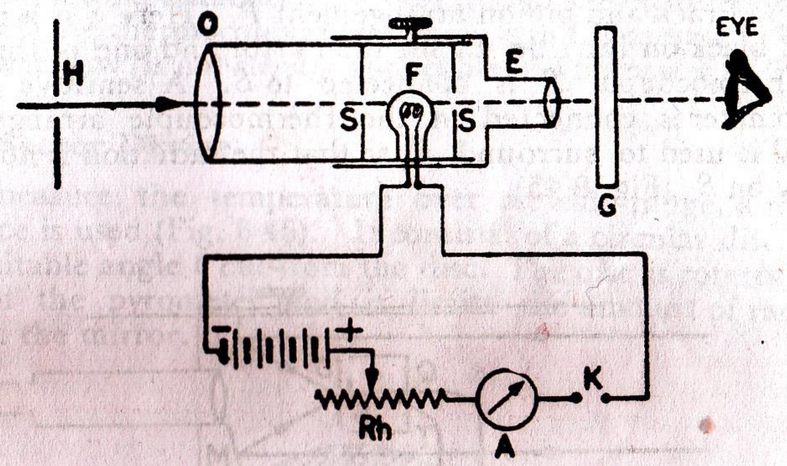


Fig. 8·44

It consists of a telescope and its cross wires are replaced by the filament F of the electric lamp (Fig. 8·44). The filament is heated with the help of a battery and the current passing through it can be adjusted with the help of a rheostat. S, S are two diaphragms and O and E are the objective and the eye-piece respectively. The filament is viewed through the eye-piece by placing red glass filter G between the eye and the eye-piece.

The radiations passing through the hole H are allowed to enter the objective of the telescope. By adjusting the position of the telescope, the hole is focussed on the filament F. The filament is visible against a background. The current through the filament is adjusted such that it begins to glow and the filament *becomes invisible* against the image of a bright hole. The red glass filter G helps in obtaining perfect matching for monochromatic radiation. The current passing through the filament, when it *disappears*, is noted. Since the brightness or heat energy emitted per sq cm is the same in the two cases, the temperature of the source from which radiations are allowed to enter the telescope is the same as that of the filament.

Initially the instrument is calibrated by taking sources at known temperatures and the corresponding currents passing through the filament are noted. A graph is plotted between the current and the temperature. From the graph, for a particular value of current passing through the filament (for disappearing position) the corresponding unknown temperature can be determined. The ammeter can also be calibrated to measure the temperatures directly.

8·41 Total Radiation Pyrometer

This pyrometer was first devised by Fery. It is used to measure the total energy of radiation of all wavelengths.

It consists of a concave mirror M made of copper and plated with nickel on the front surface. E is an eye-piece fitted at the pole of the mirror through a hole. D is a diaphragm placed in front of the mirror and at its focus. The position of M can be adjusted with the help of rack and pinion arrangement P. Here S is a metal strip painted black on the side facing the mirror and one of the junctions of a thermocouple T is connected to S. A sensitive calibrated galvanometer is connected in the thermocouple arrangement. A shield Q is used to surround S so that the radiation is not incident directly on S (Fig. 8·45).

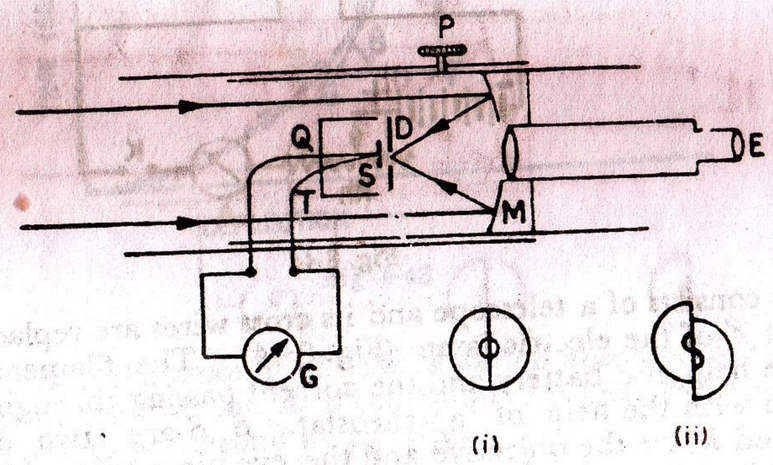


Fig. 8·45

When the radiation is incident on the mirror, the focussed image falls on the opening of D. Due to the incident radiations falling on S, the galvanometer shows a deflection. In order to focus the image accurately, the diaphragm D is made of two semicircular mirrors inclined at a small angle to each other. When the diaphragm D is viewed through the eyepiece, it appears to be circular as shown in Fig. 8 45 (i), if the focussing is accurate. If focussing is not proper, the two halves appear displaced as shown in Fig. 3·45 (ii).

The image formed on D must completely cover the aperture. The reading of the galvanometer of the thermocouple is independent of the distance of the source provided the aperture of D is completely filled by the image of the source (furnace etc.). The reading of the galvanometer depends only on the intensity of the image. If the distance of the source is doubled, the amount of radiation received by the mirror becomes one-fourth. But the area of the image is also reduced to one-fourth. Thus the intensity of the image remains the same.

Calibration

If the temperature of the source is T and that of the receiving instruments is T_0, the deflections of the galvonometer are not

proportional to $(T^4 - T_0^4)$. This is because T is large as compared to T_0. The instrument is directly calibrated with source at various temperatures. (The temperature of the source is measured with a standard thermocouple or an optical pyrometer). A graph is obtained between the logarithm of the deflection of the galvanometer and the logarithm of the absolute temperature T,

$$\log \theta = K \log T$$

The graph will be a straight line and this method gives better results. Accurate experiments show that due to the conduction along the wires of the thermocouples and stray e.m.f. generated, Stefan's fourth power law is not strictly applicable. The power of T varies from 3·8 to 4·2.

Rotating Sector Device

To measure the temperature over a wide range, a rotating sector device is used (Fig. 8·46). It consists of a circular disc with a sector of suitable angle θ cut from the disc. The disc is rotated about the axis of the pyrometer and it limits the amount of radiation incident on the mirror.

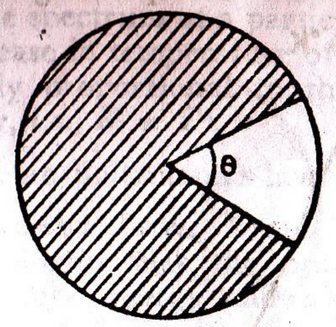


Fig. 8·46

Let T be the temperature of the source and T_1 the temperature measured with the instrument. Then

$$\frac{T^4}{T_1^4} = \frac{360}{\theta}$$

$$T^4 = \frac{T_1^4\ (360)}{\theta}$$

$$T = T_1\left[\frac{360}{\theta}\right]^{\frac{1}{4}}$$

8·42 Distribution of Energy in the Spectrum of a Black Body

Lummer and Pringsheim investigated the distribution of energy amongst the different wavelengths of a thermal spectrum of a black body radiation (full emitter).

The experimental arrangement consists of a carbon tube heated electrically [Fig. 8·47]. The radiations from this tube are allowed to

be incident on a reflector M_1 through a slit S_1. The parallel reflected beam is dispersed by a fluorspar prism. The dispersed beam is

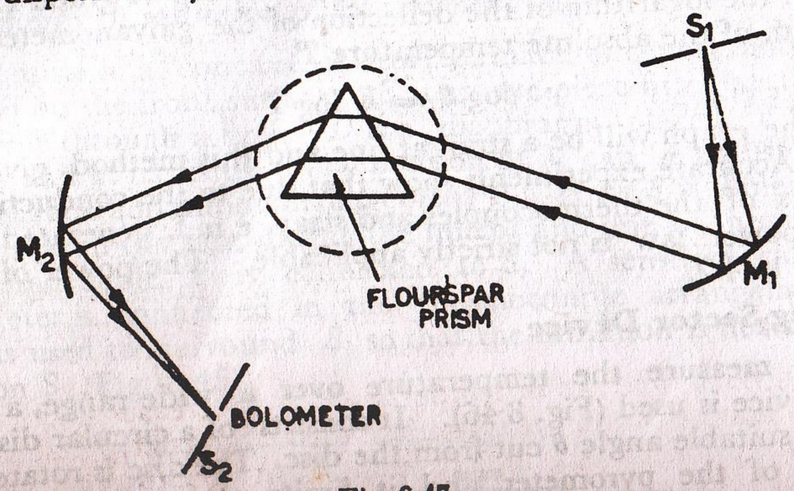


Fig. 8·47

focussed on a line bolometer with the help of the mirror M_2. The intensity of the radiations corresponding to different wavelengths

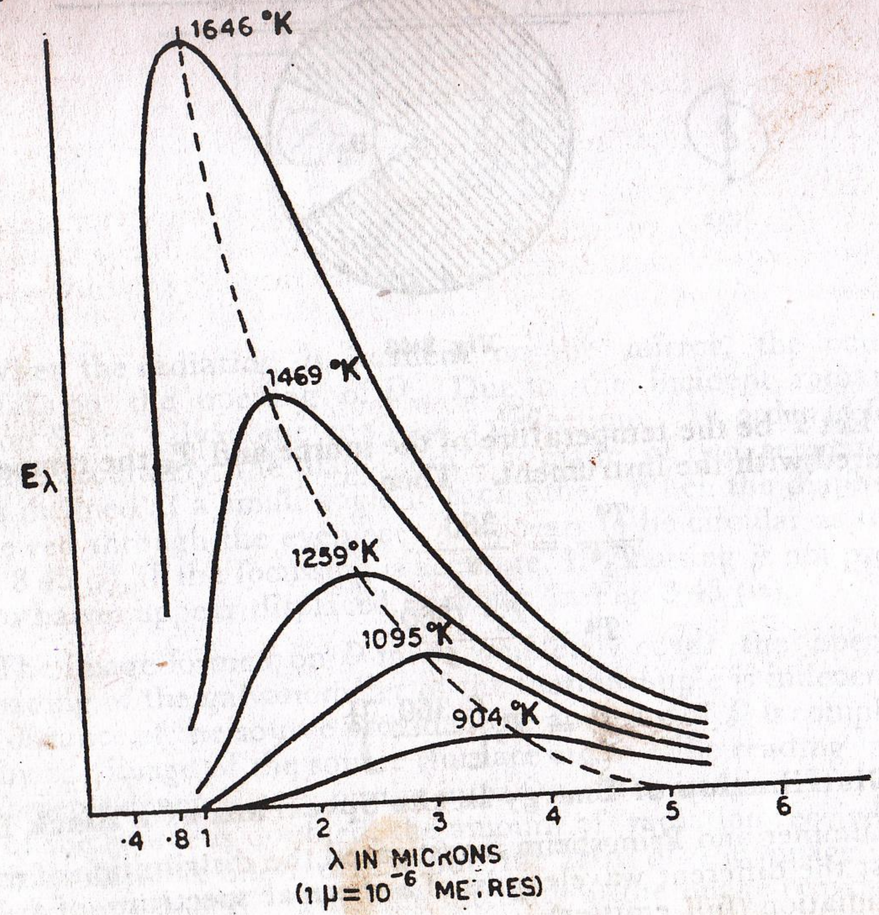


Fig. 8·48

is measured with the bolometer. The deflection in the galvanometer (of the bolometer) is proportional to the energy of the heat radiations.

To find the energy distribution for different wavelengths the fluorspar prism is gradually rotated.

The results obtained by Lummer and Pringsheim are shown in Fig. 8·48. Each curve represents the intensity of the radiations (E_λ) with wavelength for a given temperature of the source.

Results. (*i*) At a given temperature, the energy is not uniformly distributed in the radiation spectrum of a hot body.

(*ii*) At a given temperature the intensity of heat radiations increases with increase in wavelength and at a particular wavelength its value is maximum. With further increase in wavelength the intensity of heat radiations decreases.

(*iii*) With increase in temperature, λ_m decreases. Here λ_m is the wavelength at which maximum emission of energy takes place. The points on the dotted line represent λ_m at various temperatures.

(*iv*) For all wavelengths, an increase in temperature causes an increase in the energy emission.

(*v*) The area under each curve represents the total energy emitted for the complete spectrum at a particular temperature. This area increases with increase in temperature of the body. It is found that the area is directly proportional to the fourth power of the temperature of the body, *i.e.*, $E \propto T^4$.

This represents Stefan-Boltzmann's law.

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

$$\lambda_m \times T = \text{constant} = 0{\cdot}2892 \text{ cm-K} \qquad \ldots(i)$$

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

$$E_m \propto T^5$$
$$E_m = \text{constant} \times T^5 \qquad \ldots(ii)$$

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

$$E_\lambda = \lambda^{-5} f(\lambda T) \qquad \ldots(iii)$$

With certain assumptions Wien was able to deduce the relation

$$f(\lambda T) = C_1 e^{-\frac{C_2}{\lambda T}}$$

$$\therefore \qquad E_\lambda = C_1 \lambda^{-5} e^{\frac{C_2}{\lambda T}} \qquad \ldots(iv)$$

Here C_1 and C_2 are constants.

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

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

$$E_\lambda = \frac{8\pi\, kT}{\lambda^4} \qquad \ldots(v)$$

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 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 $h\nu$, $2h\nu$, $3h\nu$....., etc. He deduced the formula,

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

Here c is the velocity of electromagnetic waves ($=3\times10^8$ metres per second).

Equation (vi) agrees with the experimental results.

(i) For shorter wavelengths

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

From equation (vi),

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

A.

$$E_\lambda = C_1\, \lambda^{-5}\, e^{-\frac{C_2}{\lambda T}} \qquad \ldots(vii)$$

where $C_1 = 8\pi\, hc$ and $C_2 = \dfrac{hc}{\lambda}$

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

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

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

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

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

$$E_\lambda = \frac{8\pi kT}{\lambda^4} \qquad \ldots(viii)$$

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

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

8·43 Solar Constant

The sun is the source of heat radiations 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 the 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 distance 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 constant, S_0 the true solar constant and Z the altitude (angular elevation) of the sun, then

$$S = S_0\, a^{\sec Z} \qquad \ldots(i)$$

or

$$\log S = \log S_0 + \sec Z \log a \qquad \ldots(ii)$$

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.

8·44 Temperature of the Sun

The sun consists of a central hot portion surrounded by the photosphere. The central portion has a temperature of the order

of 10^7 K. The photosphere has a temperature of about 6000 K. This temperature is also called the effective temperature of the sun. Considering the sun as a perfect black body radiator, the temperature of the sun can be calculated.

Let the mean distance of the sun from the earth be R and S the solar constant. Then, the total amount of heat energy received by the sphere of radius R in one minute $= 4\pi R^2 S$.

If r is the radius of the sun, then the amount of heat energy radiated by 1 sq cm surface of the sun in one minute

$$E = \frac{4\pi R^2 S}{4\pi r^2} = \left(\frac{R}{r}\right)^2 \times S$$

Taking $R = 148{\cdot}48 \times 10^7$ km

$r = 6{\cdot}928 \times 10^5$ km

The mean value of

$S = 1{\cdot}94$ cals per cm² per minute.

$$E = \left(\frac{148{\cdot}48 \times 10^7}{6{\cdot}928 \times 10^5}\right)^2 \times \frac{1{\cdot}94}{60} \text{ cals per second} \quad \ldots(i)$$

Also $E = \sigma T^4$

But $\sigma = 5{\cdot}75 \times 10^{-5}$ ergs per cm² per second

$$= \frac{5{\cdot}75 \times 10^{-5}}{4{\cdot}2 \times 10^7} \text{ cal per cm}^2 \text{ per second}$$

$$E = \frac{5{\cdot}75 \times 10^{-5}}{4{\cdot}2 \times 10^7} \cdot T^4 \quad \ldots(ii)$$

Equating (i) and (ii)

$$\left(\frac{5{\cdot}75 \times 10^{-5}}{4{\cdot}2 \times 10^7}\right) T^4 = \left(\frac{148{\cdot}48 \times 10^7}{6{\cdot}928 \times 10^5}\right)^2 \times \frac{1{\cdot}94}{60}$$

$$T = 5730 \text{ K} \quad \ldots(iii)$$

This temperature gives the effective temperature of the sun acting as a black body radiator. The actual temperature of the sun is higher than this value. The temperature of the sun is usually taken as 6000 K.

Temperature of the sun can also be calculated from Wien's displacement law,

$$\lambda_{max} T = 0{\cdot}2892$$

The wavelength of the radiations for which the energy is maximum in the spectrum is 4900×10^{-8} cm.

Substituting the value of λ_m, the value of T comes out to be 5902 K. This value is in agreement with the accepted value. Hence, the effective temperature of the sun (photosphere) is about 6000 K.

Example 8·13. *Calculate the black body temperature of the sun from the following data :* (*Punjab 1966 ; Delhi 1971*)

Stefan's constant $= 1{\cdot}37 \times 10^{-12}$ cal/cm²/s

Solar constant $= 2{\cdot}3$ cal/cm²/minute

Radius of the sun $= 7 \times 10^{10}$ cm

Distance between the sun and the earth $= 1{\cdot}5 \times 10^{13}$ cm

$$E = \frac{4\pi R^2 S}{4\pi r^2} = \left(\frac{R}{r}\right)^2 . S$$

Here $R = 1{\cdot}5 \times 10^{13}$ cm

$r = 7 \times 10^{10}$ cm

$S = 2{\cdot}3$ cal/cm²/minute

$$E = \left[\frac{1{\cdot}5 \times 10^{13}}{7 \times 10^{10}}\right]^2 \times \frac{2{\cdot}3}{60} \text{ cal/s} \quad \ldots(i)$$

$$E = \sigma T^4 \quad \ldots(ii)$$

Equating (i) and (ii),

$$\sigma T^4 = \left[\frac{1{\cdot}5 \times 10^{13}}{7 \times 10^{10}}\right]^2 \times \frac{2{\cdot}3}{60}$$

$$1{\cdot}37 \times 10^{-12} \times T^4 = \left[\frac{1{\cdot}5 \times 10^{13}}{7 \times 10^{10}}\right]^2 \times \frac{2{\cdot}3}{60}$$

$$T = \mathbf{5987\ K}$$

8·45 Angstrom's Pyrheliometer

Pyrheliometer is an instrument which is used to find the amount of incidient heat radiations and the solar constant. Angstrom's pyrheliometer consists of two identical strips A and B of blackened platinum foil (Fig. 8·49).

The strip A is exposed to the sun and B is shielded by a cover C. A thermocouple having a sensitive galvanometer with A as one junction and B as the other junction is used. The strip B can be heated by an electrical arrangement and suitable current passing through B can be adjusted with the help of a rheostat.

When both the strips A and B are shielded from the sun, their junctions are at the same temperature and the galvanometer shows no deflection. The strip A is exposed to the sun and B is kept shielded. The strip A receives heat radiations from the sun and its temperature rises and the galvanometer shows deflection. The strip B is gradually heated by passing current through it and the current is adjusted so that there is no deflection in the galvanometer.

It means the strips A and B are again at the same temperature and they are receiving heat energy at the same rate.

Let H calories of heat be incident on one sq cm surface of the strip in one minute. The area of the plate $A = A$ sq cm and absorption coefficient $= a$.

The amount of heat radiations absorbed in one minute by the plate $A = H\ Aa$ calories. $\ldots(i)$

Heat produced in one minute in the strip B

$$= \frac{EI \times 60}{4{\cdot}2} \text{ cal} \qquad \ldots(ii)$$

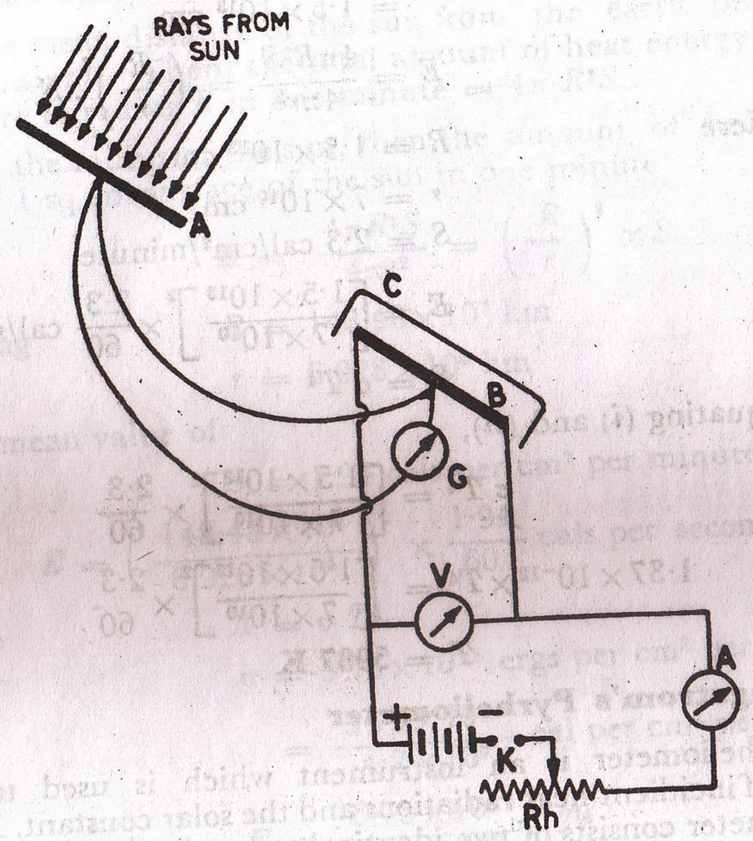


Fig. 8·49

Here E volts is the potential difference across the strip B and I amperes is the current flowing through it.

Equating (i) and (ii),

$$HAa = \frac{EI \times 60}{4{\cdot}2} \qquad \ldots(iii)$$

Hence H can be calculated.

8·46 Water Flow Pyrheliometer

This instrument was designed by Abbot and Fowle. It consists of a cylindrical doubled walled vessel A. The lower side is conical in shape and is coated with platinum black on its inner side. Water can be circulated through the walls at a constant rate. 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 state has been reached *i.e.*, T_1 and T_2 show constant temperatures, the heat radiations from the sun are cut off.

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

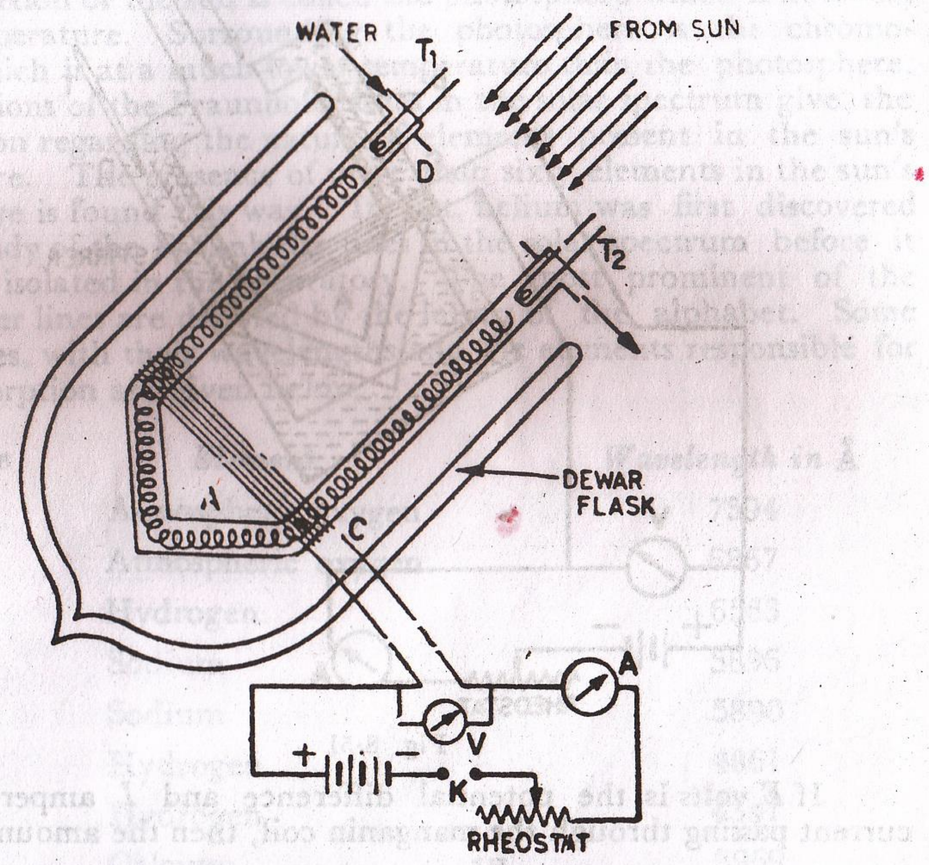


Fig. 8·50

second $= \frac{EI}{4{\cdot}2}$ cal. Therefore, the amount of heat radiations received from the sun in one minute by the exposed surface of the vessel $A = \frac{EI \times 60}{4{\cdot}2}$ cal. From this value, the solar constant can be calculated.

8·47 Water Stir Pyrheliometer

In this type of pyrheliometer the heat radiations are received from the sun by the conical end of the vessel A, which is coated with lamp black. Vessel A is surrounded by a calorimeter D containing water. The stirrer helps in circulating water vigorously and is driven by an electric motor. The temperature of water is measured with the help of a platinum resistance thermometer P, whose wire is wound around A (Fig. 8·51). Heat radiations from the sun are

allowed to enter the vessel *A* and the rise in temperature of water in one second is calculated. The heat radiations are cut off and a suitable current is passed through the manganin coil *C* for a known time so that the rise in temperature of water in one second is the same.

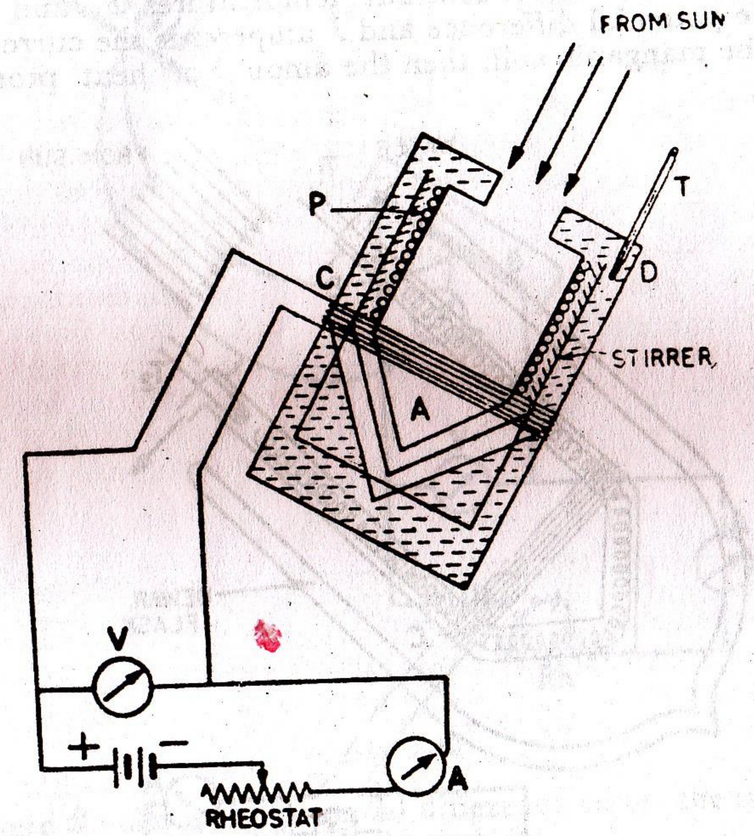


Fig. 8·51

If *E* volts is the potential difference and *I* amperes is the current passing through the manganin coil, then the amount of heat produced per second $= \frac{EI}{4{\cdot}2}$ cal. Therefore, the amount of heat radiations received from the sun in one minute by the exposed surface of the vessel $A = \frac{EI \times 60}{4{\cdot}2}$ cal. From this value, the solar constant can be calculated.

8·48 Solar Spectrum

The radiation received from the sun is similar to that of a perfectly black body. In a solar spectrum the wavelength corresponding to maximum energy is about 5000 Å for a surface temperature of 5750 K. The solar spectrum consists of a large number of dark lines called **Fraunhofer lines**. These lines were first observed by Wollaston in 1802 and later studied by Fraunhofer in 1814. These lines are observed in the complete range of the spectrum *viz.* ultra-violet, visible and infrared. Fraunhofer measured the wavelengths of many of these lines accurately and found that they

occupied exactly the same positions as the bright lines emitted by different gases and vapours.

According to Kirchhoff's law of radiation, any substance at a lower temperature will absorb the radiations of those wavelengths which it will emit when excited by electric discharge. Thus the solar spectrum is an absorption spectrum and the Fraunhofer lines are the absorption lines of relatively cooler gases and vapours present in the earth's atmosphere and the sun's outer atmosphere. The central portion of the sun is called the photosphere which is at a very high temperature. Surrounding the photosphere is the chromosphere which is at a much lower temperature than the photosphere. The positions of the Fraunhofer lines in the solar spectrum give the information regarding the nature of elements present in the sun's atmosphere. The presence of more than sixty elements in the sun's atmosphere is found this way. In fact, helium was first discovered by the study of the Fraunhofer lines in the solar spectrum before it had been isolated in the laboratory. The most prominent of the Fraunhofer lines are denoted by the letters of the alphabet. Some of the lines, with their wavelengths and the elements responsible for their absorption are given below :

Line	*Element*	*Wavelength in* Å
A	Atmospheric oxygen	7594
B	Atmospheric oxygen	6867
C	Hydrogen	6563
D_1	Sodium	5896
D_2	Sodium	5890
F	Hydrogen	4861
G_1	Hydrogen	4341
H	Calcium	3969
K	Calcium	3934

8·49 Infra-red Spectrum

Extending on either side of the visible spectrum, there are invisible radiations which do not cause the sensation of sight. The radiations beyond the red end of the visible spectrum are called infra-red radiations and their wavelengths extend up to 400,000 Å. Sun is a powerful source of infra-red radiation. Beyond the violet end of the visible spectrum, the radiations extending up to a wavelength of 100 Å are called ultraviolet radiations.

The heating effect of the infra-red radiations is used in measuring the wavelength of the radiation. An infra-red ray spectrometer is shown in Fig. 8·52. Light from a strong source of light such as an electric arc is rendered parallel by reflection from a concave stainless steel mirror M_1. This parallel beam is refracted through the rock salt prism *P* and the emergent dispersed beam

after reflection from the mirrors M_1 and M_3 is incident on a thermopile or a bolometer. M_2 is a plane mirror and M_3 is a concave mirror. Wien's law of radiation is given by

$$\lambda_m T = 0{\cdot}2892$$

where T is the absolute temperature and λ_m is the wavelength of the radiation. The thermopile readings help in the calculation of temperature and from the temperature, λ can be calculated.

As infra-red radiations are not absorbed by air or thick frog, infra-red ray photographs can be taken over long distances of fog and mist where visible light cannot penetrate. For this, specially designed photographic plates are used with suitable filters. A solution of iodine in alcohol is a suitable filter, because this transmits the infra-red radiations and absorbs the visible light. In the World War II, infra-red photography played a very useful part in detecting objects in the dark through mist, fog and clouds. Infra-red radiations have a wide application in the field of medicine, industry etc. Infra-red radiations can penetrate deep into the human body and by their property of heating can dilate the blood vessel at the portion exposed to the radiations. This enables increased flow of blood.

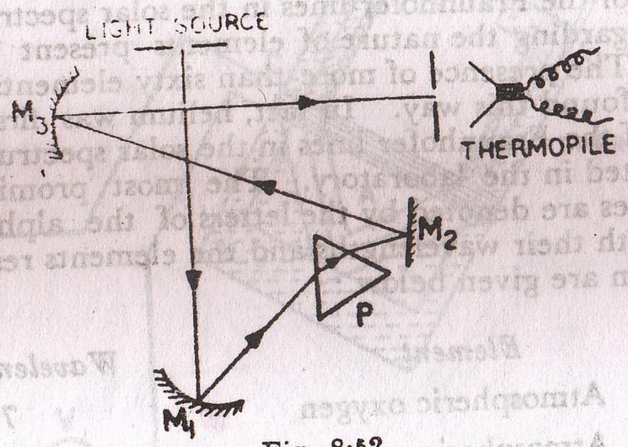


Fig. 8·52

8·50 Ultra-violet Spectrum

The spectrum that covers the wavelengths from 4000Å to 100Å is called the ultra-violet spectrum. Sun is a natural source of light rich in ultra-violet radiations. An electric arc of carbon, iron or other materials, mercury vapour lamps, discharge of electricity

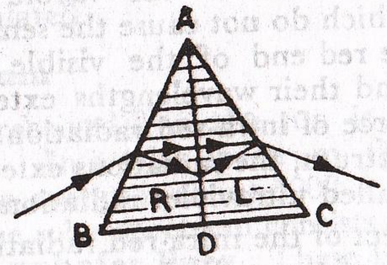


Fig. 8·53

through hydrogen contained in quartz tubes are some of the artificial sources that give ultra-violet radiations.

Ordinary glass absorbs the ultra-violet radiations. Hence quartz lenses and prisms are used. But quartz is a doubly refracting material. If a single prism of quartz is used, due to the property of double refraction of the prism, two images of the slit (ordinary and extraordinary) corresponding to a single wavelength are observed. This will reduce the sharpness of each image. To compensate for this, the collimating lens is made from right-handed quartz and the telescope objective is made from left-handed quartz. Similarly the prism used for the dispersion of the incident beam consists of two halves. The two halves are held together by glycerine. One half is made from right-handed quartz and the other half is made from left-handed quartz.

In Fig. 8·53, *ABD* is a right-angled prism of right-handed quartz and *ADC* is of left-handed quartz. For recording an ultra-violet spectrum for wavelengths shorter than 1,200Å, a concave reflection grating is used. The diffracted beam is photographed. The grating and the photographic plate are enclosed in a metal chamber which is evacuated.

Ultra-violet radiations have a variety of applications. Sterilisation of rooms in which blood plasma, drugs, vaccines etc. are prepared and sealed in the containers is done by ultra-violet radiations. Drugs, poisons, dyes etc. fluoresce under the action of ultra-violet rays. The resolving power of a microscope is increased when ultra-violet light is used for illumination. Fluorescent tubes depend on the principle of fluorescence effected by ultra-violet radiations.

8·51 Electromagnetic Spectrum

Visible spectrum includes those wavelengths which can stimulate the sense of sight. But there is no basic difference between light waves and the electromagnetic waves produced by electrical oscillating circuits. The term electromagnetic spectrum is used for the range of wavelengths from 10^4 metres to 1Å (10^{-8} cm). There is in fact no limit to the production of electromagnetic waves of very long wavelengths. The frequency of an alternating current generator can be made as low as possible by decreasing the speed of the generator. The wavelength of waves transmitted by a 50 cycle transmission line is 5×10^8 cm. Waves of shorter wavelength can be produced by electrical oscillators. X-rays and gamma rays represent the waves of very short lengths. The complete electromagnetic spectrum is shown in the table at page 426.

It is interesting to note that the visible range of the spectrum comprises only a small range of the electromagnetic spectrum extending approximately from 4000Å in the extreme violet region to 8000Å in the extreme red. Beyond the violet region of the visible spectrum is the ultraviolet, the X-rays and γ-rays. Beyond the red

end of the visible spectrum are the short radio waves and radio broadcast waves.

ELECTROMAGNETIC SPECTRUM

	WAVELENGTHS (IN VACUUM)		
	ANGSTROM UNITS	cm	METRES
X-RAYS AND γ RAYS	1 – 10		
ULTRA-VIOLET	10^2 – 10^3		
VISIBLE			
INFRA-RED	10^4 – 10^5 – 10^6	10^{-4} – 10^{-3} – 10^{-2} – 10^{-1}	
SHORT RADIO WAVES		1 – 10 – 10^2	10^{-2} – 10^{-1} – 1 – 10 – 10^2
RADIO BROADCAST WAVES			10^3 – 10^4

Exercises VIII

1. Describe Lee's method to find the coefficient of thermal conductivity of metals.

2. Discuss the rectilinear flow of heat along a bar of uniform area of cross-section.

(Berharmpur 1972, Bombay 1974)

3. Discuss Ingen-Hausz experiment to compare the thermal conductivity of different materials.

4. Discuss in detail Forbes method for finding the coefficient of thermal conductivity of a metal bar. *(Delhi 1976)*

5. Discuss Lee and Charlton's method for finding the coefficient of thermal conductivity for bad conductors. *(Delhi 1977)*

6. Give the theory of radial flow of heat.

7. Discuss the cylindrical flow of heat. Describe experiments to find the coefficients of thermal conductivity of glass and rubber.

8. Discuss the heat flow through a compound wall.

9. Discuss "accretion of ice" on ponds.

10. Discuss Wiedemann-Franz law.

11. Show how the atmospheric pressure changes with height. Calculate the lapse rate.

12. What do you understand by a black body ? State and explain Kirchhoff's laws of heat radiations.

(Berhampur 1972, Delhi 1976)

13. State Stefan's law of heat radiation and derive the law mathematically.

14. Describe an experiment for the verification of Stefan's law. *(Lucknow 1964)*

15. Give a laboratory method for determining the Stefan's constant. What is its numerical value in M.K.S. units ?

(Lucknow 1965)

16. Describe the working of (*i*) disappearing filament pyrometer, (*ii*) total radiation pyrometer and (*iii*) pyrheliometer.

17. Discuss the distribution of energy in the spectrum of a black body. What are the results obtained by Lummer and Pringsheim ?

18. Discuss Wien's displacement law and Raleigh-Jeans law. How is Planck's law applicable for all wavelengths ?

(Delhi 1971)

19. Describe the cylindrical shell method of determining the thermal conductivity of poor conductors. Derive the formula you will use. *(Lucknow 1963)*

20. Describe Lee's method for determining the thermal conductivity of poor conductors. *(Ag. 1963)*

21. What is Stefan's law of radiation ? Give a laboratory method for determining Stefan's constant. *(Delhi 1977)*

22. What is meant by black body radiation ? State and prove Stefan's law. *(Agra 1966)*

23. Describe Planck's law of black body radiation. Describe an experiment to verify the law. *(Delhi 1967)*

24. Deduce Stefan's law of radiation from the principles of thermodynamics. Describe an experiment to determine Stefan's constant.

(Bombay 1974, Gorakhpur 1967, Delhi 1976)

25. Give an account of the methods for measuring high temperatures by radiation pyrometry.

(Gorakhpur 1967, Delhi 1971)

26. Describe with necessary theory a method of comparing the conductivities of two metals. *(Gorakhpur 1967)*

27. Describe Lee's method for determining the thermal conductivity of bad conductors. *(Calcutta 1966)*

28. Define a perfectly black body. Show that an enclosure maintained at a constant temperature behaves as a perfectly black body irrespective of the nature of the walls or the interior. Describe a black body in practice.

(Rajasthan 1966, Delhi 1971)

29. What is black body radiation ? State Stefan's law and describe a method for determining Stefan's constant. *(Delhi 1969)*

30. Describe the construction and working of a total radiation pyrometer. *(Delhi 1972)*

31. Define thermal conductivity and give its units. Describe Lee's method of determining the thermal conductivity of a bad conductor. *(Delhi 1973)*

32. Explain what you understand by a black body. State Stefan's law of radiation and prove it from thermodynamical considerations. Indicate how it can be verified. How is this law distinguished from Newton's law of cooling ?

(Delhi 1975)

33. Describe in detail a suitable experimental method of determining the thermal conductivity of a bad conductor.

(Delhi 1975)

34. Prove that for an atmosphere in convective equilibrium, the rate of fall of temperature with altitude for dry air is given by the expression

$$\frac{dT}{dh} = \frac{-Mg(\gamma-1)}{R\gamma}$$

(Delhi, 1974)

35. Define coefficient of thermal conductivity. Describe Forbes' method for determining the thermal conductivity of a metal rod. Mention some of the limitations of this method. *(Delhi 1974, 1976)*

36. Prove that at any temperature, the ratio of the emissive power to the absorptive power of a surface is constant and is equal to the emissive power of a perfectly black body. *(Delhi 1974)*

37. Derive Planck's radiation formula and show that Raleigh-Jean's law and Wien's law are special cases of Planck's law. *(Delhi 1974)*

38. State and explain the laws relating to radiation and temperature of a radiating body. What do you mean by

(*a*) perfectly black body,

(*b*) coefficient of absorption and

(*c*) coefficient of emission ? *(Delhi 1976)*

39. Define solar constant. How is it experimentally determined ? Comment on the source of energy in the sun. *(Kanpur 1975)*

40. Define coefficient of thermal conductivity. What do you understand by a thermal steady state ? *[Delhi, 1978]*

41. Describe Forbes' method for the determination of thermal conductivity of a metal rod. Mention the merits and limitations of this method. *[Delhi, 1978]*

42. State and prove Kirchhoff's law of thermal radiation. Mention one of its illustrative examples. *[Delhi, 1978]*

43. State the basic concept on which Planck's law of black-body radiation is based. Write down Planck's formula and show that Wien's and Rayleigh-Jeans laws are particular cases of it. *[Delhi, 1978]*

44. What is quantum theory of radiation ? Derive Planck's formula for the distribution of energy in the spectrum of a black body. Deduce from it Wien's displacement law and Rayleigh-Jeans law. *[Delhi (Hons.), 1978]*

45. Find the time in which a layer of ice 6 cm thick on the surface of a pond will increase its thickness by 2 mm, when the temperature of the surrounding air is −20°C.

$K = 0{\cdot}005$, $L = 80$ cal/g, $\rho = 0{\cdot}91$ g/cm^3

[Ans. 13 min 48·16 s]

46. How much time will it take for a layer of ice of thickness 8 cm to increase by 4 cm on the surface of a pond when the temperature of the surroundings is −10°C.

$K = 0{\cdot}005$, $L = 80$ cal/g, $\rho = 0{\cdot}90$ g/cm^3

[Ans. 16 hours]

47. Two large closely spaced concentric spheres (both of which are black body radiators) are maintained at temperatures of 400 K and 600 K respectively. The space in between the two spheres is evacuated. Calculate net rate of energy transfer between the two temperatures.

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units

[Ans. 5·90 kilowatts/m^2]

48. Calculate the radiant emittance of a black body at a temperature of (*i*) 200 K and (*ii*) 2000 K.

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units

[**Ans.** (*i*) 90·75 watts/m² (*ii*) 907·5 kilowatts/m²]

49. The relative emittance of tungsten is approximately 0·70. A tungsten sphere of surface area 5×10^{-4} sq metres is suspended inside a large evacuated enclosure whose walls are at 300 K. What power input is required to maintain the sphere at a temperature of 3000 K. The conduction of heat along the supports can be neglected.

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units.

[**Ans.** 1609 watts]

50. An aluminium foil of relative emittance 0·2 is placed in between two concentric spheres at temperatures 300 K and 200 K respectively. Calculate the temperature of the foil after the steady state is reached. Assume that the spheres are perfect black body radiators. Also calculate the rate of energy transfer between one of the spheres and the foil.

$\sigma = 5{\cdot}672 \times 10^{-8}$ M.K.S. units.

[**Ans.** (*i*) 263·8 K, (*ii*) 37 watts/m²]

51. Calculate the energy radiated per minute from the filament of an incandescent lamp at 3000 K, if the surface area is 10^{-4} sq metres and its relative emittance is 0·425. [**Ans.** 11710 joules]

52. An iron furnace radiates $7{\cdot}65 \times 10^4$ calories per hour through an opening of cross section 10^{-4} sq metres. If the relative emittance of the furnace is 0·40, calculate the temperature of the furnace. [**Ans.** 2500 K]

53. Write notes on : *(Delhi 1972)*

(*i*) Planck's law

(*ii*) Raleigh-Jean's law

(*iii*) Wien's displacement law. *(Delhi (Hons). 1976 ; Berhampur 1972)*

(*iv*) Convective Equilibrium of the atmosphere. [*Delhi 1972, 73, 75 Delhi (Hons.) 1971, 77)*

(*v*) Optical pyrometer *(Delhi 1975)*

(*vi*) Radiation pyrometer *(Delhi 1974, 75, 77)*

(*vii*) Black body radiation *(Delhi 1975)*

(*viii*) Radiation Pyrometry. *(Delhi (Hons.) 1977)*

9

Statistical Thermodynamics

9·1 Statistical Mechanics

Statistical mechanics deals with systems consisting of many particles and the methods employed are to get a collective or macroscopic property of the system without taking into account the individual motion of the particles. The word particle is used in a broad sense meaning a fundamental particle *e.g.* an electron, an atom, a molecule etc. The particle is a well defined and a stable unit of a given physical system. As it is not practically possible to determine the property of each particle individually, a statistical approach is made by using the concept of probability of distribution. This statistical approach helps in determining the bulk or macroscopic property of the system as a whole. The idea of probability does not imply that the particles move in a random way without obeying the laws. For a many particle system, the statistical analysis is valid regarding the applications of probability distribution of particles.

9·2 Statistical Equilibrium

Consider that a thermodynamical isolated system consists of N particles. The energy states available to the particles are E_1, E_2, E_3 etc. These energy states may be quantized or may be continuous and are due to vibrational and rotational energy of the particles.

Suppose, that at any given instant of time, n_1 particles are in state of energy E_1, n_2 particles with energy state E_2 and so on.

The total number of particles in the system is,

$$N = n_1 + n_2 + n_3 + \ldots\ldots = \sum_i n_i \qquad \ldots(i)$$

Here $i = 1, 2, 3$ etc.

The total energy of the system,

$$U = n_1E_1 + n_2E_2 + n_3E_3 + \ldots\ldots$$

$$U = \sum_i n_i E_i \qquad \ldots(ii)$$

Equation (*ii*) refers to the total energy of a system in which the particles are non-interacting. Here, the energy of each particle depends only on the coordinates of the particle in the system. For an isolated system, the total energy U is constant.

For isolated system.

$$U = \sum_i n_i E_i = \text{constant} \qquad \ldots(iii)$$

Consider a gas having N molecules at a certain temperature and pressure. Its volume, temperature and pressure are kept constant *i.e.* the system is isolated. The total energy of this system remains constant. But, the molecules of the gas collide with each other and also with the walls of the container. Consequently, the number of molecules change from one energy state to the other energy state. It means that the value of n_1, n_2, n_3 etc. continuously change. It can be reasonably assumed that for each microscopic state of a system of particles, there is a particular most favoured distribution. When this distribution or partition is reached, the system attains statistical equilibrium. For an isolated system, the values of n_0, n_1, n_3 etc. vary only near the values corresponding to the most probable distribution. Hence, the basic problem in statistical thermodynamics is to obtain the most probable distribution law for a given composition of the system.

In practice, three most probable distribution laws are used. They are

(*i*) Maxwell-Boltzmann Distribution Law

(*ii*) Fermi-Dirac Distribution Law (Statistics)

(*iii*) Bose-Einstein Distribution Law (Statistics).

9·3 Probability theorems in Statistical Thermodynamics

The following are the important probability theorems commonly used in statistical thermodynamics :

(1) The number of ways in which N distinguishable particles can be arranged in order is equal to

$$N\,!$$

(2) The number of different ways in which n particles can be selected from N distinguishable particles irrespective of the order of selection is equal to

$$\frac{N\,!}{(N-n)\,!\,n\,!}$$

(3) The number of different ways in which n indistinguishable particles can be arranged in g distinguishable states with not more than one particle in each state is equal to

$$\frac{g\,!}{n\,!\,(g-n)\,!}$$

9·4 Maxwell-Boltzmann Distribution Law

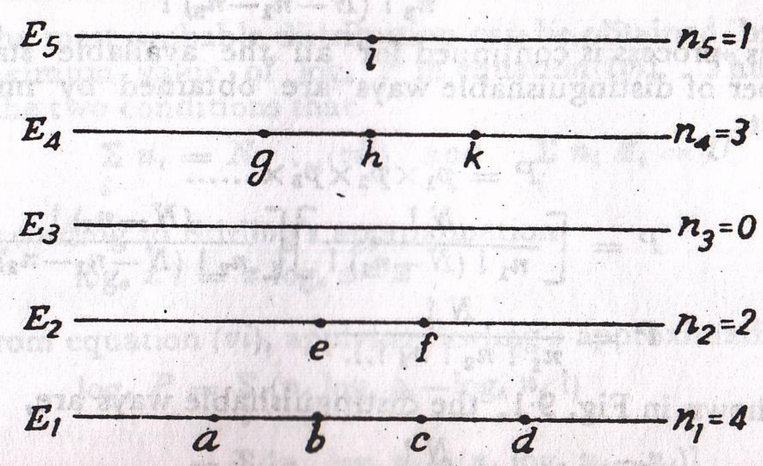


Fig. 9·1

Consider a system that contains a large number of particles that are *identical* and *distinguishable*. The identical particles refer to the particles having the same structure. The distinction between the particles is due to their energy states at a given instant. As shown in Fig. 9·1, 4 particles are in energy state E_1, 2 in state E_2, zero in state E_3 and so on. It is assumed that all the energy states are accessible to each particle. Consequently, it can be assumed that the probability of any particular partition is proportional to the number of different ways in which the particles can be distributed in the existing available energy states so as to produce the desired partition.

To obtain the required distribution as shown in Fig. 9·1, the first particle a in state E_1 can be selected in N ways. The second particle b in state E_1 can be selected in $(N-1)$ ways and so on. Therefore, the total number of ways in which the first four particles in state E_1 can be selected is given by,

$$N(N-1)\,(N-2)\,(N-3) = \frac{N\,!}{(N-4)\,!}$$

Moreover, the four particles in state E_1 can be arranged in 4! different orders. For example, *abcd*, *bcda*, *cdab* and so on. There are 24 ways. But, it is immaterial for these particles to be arranged in any particular order in state E_1, because they are identical. Thus, the total number of *distinguishable* different ways are,

$$\frac{N\,!}{4\,!\,(N-4)\,!}$$

In general, if the first state consists of n_1 particles, the distinguishable different ways, for arranging n_1 particles in state E_1, are,

$$p_1 = \frac{N\,!}{n_1\,!\,(N-n_1)\,!} \qquad \ldots(i)$$

For the second state E_2, only $(N-n_1)$ particles are available and n_2 particles are in state E_2. The number of distinguishable different ways are,

$$p_2 = \frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)!} \qquad ...(ii)$$

If this process is continued for all the available states, the total number of distinguishable ways are obtained by multiplying p_1, p_2, p_3 etc.

$$\therefore \quad P = p_1 \times p_2 \times p_3 \times .....$$

$$P = \left[\frac{N!}{n_1!\,(N-n_1)!}\right]\left[\frac{(N-n_1)!}{n_2!\,(N-n_1-n_2)}\right]\times .....$$

$$P = \frac{N!}{n_1!\,n_2!\,n_3!...} \qquad ...(iii)$$

As shown in Fig. 9·1, the distinguishable ways are,

$$P = \frac{N!}{4!\,2!\,0!\,3!\,1!} \qquad ...(iv)$$

Here 0 ! is equal to one.

It has been assumed so far that all the available states have the same probability of occupation by the particles. However, it may happen that the states have different intrinsic probabilities say g_i. For example, a particular energy state may be favourable with more different angular momentum states than the rest and hence it is more likely to be occupied. Taking into account this intrinsic probability factor, the value of P will be different.

If g_i is the probability of locating a particle in a certain energy state E_i, then the probability of locating 2 particles in the same state is $g_i \times g_i = g_i^2$. For n_i particles, the probability is $g_i^{n_i}$. Hence the total probability for a given distribution is given by

$$P = \frac{N!\,g_1^{n_1}\,g_2^{n_2}\,g_3^{n_3}.....}{n_1!\,n_2!\,n_3!\,n_4!.....} \qquad ...(v)$$

Here n_1, n_2, n_3 etc. are the number of particles in states E_1, E_2, E_3, etc. and g_1, g_2, g_3 etc. are the intrinsic probabilities for states E_1, E_2, E_3 etc.

If all the particles are further assumed to be indistinguishable i.e. particles in state E_i and particles in state E_i cannot be distinguished, then $N!$ permutations among the particles themselves and occupying the different states result in the same distribution. The probability in this case is given by

$$P = \frac{1}{N!}\left[\frac{N!\,g_1^{n_1}\,g_2^{n_2}\,g_3^{n_3}.....}{n_1!\,n_2!\,n_3!.....}\right]$$

$$\therefore \quad P = \frac{g_1^{n_1}\,g_2^{n_2}\,g_3^{n_3}.....}{n_1!\,n_2!\,n_3!}$$

$$\therefore \quad P = \prod_i^N \frac{g_i^{n_i}}{n_i!} \qquad ...(vi)$$

Here Π is the product sign (since probability is the product of such distributions.

The most probable distribution can be obtained by evaluating the maximum value of $\log_e P$ in equation (vi). This should also satisfy the two conditions that

$$\sum_i n_i = N \quad ...(vii) \quad \text{and} \quad \sum_i n_i E_i = U \qquad ...(viii)$$

According to Stirling's approximation

$$\log_e x! = x \log_e x - x$$

From equation (vi), applying Stirling's approximation, we get

$$\log_e P = \sum_i (n_i \log_e g_i - \log_e n_i!)$$

$$= \sum_i [n_i \log_e g_i - (n_i \log_e n_i - n_i)]$$

$$= \sum_i (n_i \log_e g_i - n_i \log_e n_i + n_i)$$

$$= \sum_i n_i - \sum_i (n_i \log_e n_i - n_i \log_e g_i)$$

$$\log_e P = N - \sum_i n_i \log_e \frac{n_i}{g_i} \qquad ...(ix)$$

Differentiating equation (ix)

$$d(\log_e P) = -\sum_i (dn_i) \log_e \frac{n_i}{g_i} - \sum_i n_i\, d\left(\log_e \frac{n_i}{g_i}\right)$$

$$= -\sum_i dn_i \log_e \frac{n_i}{g_i} - \sum_i n_i \frac{d\,n_i}{n_i}$$

$$= -\sum_i dn_i \log_e \frac{n_i}{g_i} - \sum_i dn_i$$

But $\sum_i dn_i = 0$

$$\therefore \quad -d(\log_e P) = \sum_i \left[\log_e \left(\frac{n_i}{g_i}\right)\right] dn_i \qquad ...(x)$$

To obtain the maximum value of P, $d(\log_e P) = 0$

$$\therefore \quad \sum_i \log_e \left(\frac{n_i}{g_i}\right) dn_i = 0 \qquad ...(xi)$$

But $\Sigma\, dn_i = 0$ ...(xii)

and $\Sigma\, E_i\, dn_i = 0$ ...(xiii)

Multiplying (xii) by α and $(xiii)$ by β and adding to equation (xi), we get

$$\sum_i \left[\log_e \left(\frac{n_i}{g_i}\right) + \alpha + \beta E_i\right] dn_i = 0$$

The equilibrium distribution is possible if

$$\log_e \frac{n_i}{g_i} + \alpha + \beta E_i = 0 \qquad \ldots(xiv)$$

or $$\frac{n_i}{g_i} = e^{-\alpha - \beta E_i}$$

or $$n_i = g_i e^{-\alpha - \beta E_i} \qquad \ldots(xv)$$

This gives the maximum probability distribution and α and β are two parameters that depend upon the physical property of the system.

$$N = n_1 + n_2 + n_3 + \ldots\ldots$$

$$N = g_1 e^{-\alpha - \beta E_1} + g_2 e^{-\alpha - \beta E_2} + \ldots\ldots$$

$$N = e^{-\alpha}[g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2} + \ldots\ldots]$$

$$N = e^{-\alpha}\left[\sum_i g_i e^{-\beta E_i}\right]$$

Take $$\sum_i g_i e^{-\beta E_i} = Z \qquad \ldots(xvi)$$

Here, Z is called the partition function.

$$N = e^{-\alpha}(Z) \qquad \ldots(xvii)$$

$$\therefore \quad e^{-\alpha} = \frac{N}{Z}$$

Substituting this value in equation (vii)

$$n_i = \left(\frac{N}{Z}\right)\left[g_i e^{-\beta E_i}\right] \qquad \ldots(xviii)$$

This equation refers to Maxwell-Boltzmann distribution law.

Example 9·1. *A system consists of 6000 particles distributed in three energy states with equal spacing. The energy of the three states are $E_1 = 0$, $E_2 = x$ and $E_3 = 2x$. All the three states have the same intrinsic probability g. At a certain instant there are 3000 particles in the lower level, 2500 in the middle level and 500 in the upper level. Compare the relative probabilities with the distribution obtained by the transfer of one particle from the middle to the lower level and one particle from the middle to the upper level and the original distribution.*

Let P_1 and P_2 be the probabilities in the two cases

In the first case,

$$N = 6000,\ n_1 = 3000,\ n_2 = 2500,\ n_3 = 500$$

$$P_1 = \frac{g^N}{n_1 ! \, n_2 ! \, n_3 !}$$

$$P_1 = \frac{g^{6000}}{3000 ! \, 2500 ! \, 500 !} \qquad \ldots(i)$$

In the second case

$$N = 6000$$

$$n_1 = 3001,\ n_2 = 2498,\ n_3 = 501$$

$$\therefore \quad P_2 = \frac{g^{6000}}{3001 ! \, 2498 ! \, 501 !} \qquad \ldots(ii)$$

Dividing (ii) by (i)

$$\frac{P_2}{P_1} = \frac{3000 ! \, 2500 ! \, 500 !}{3001 ! \, 2498 ! \, 501 !}$$

$$\frac{P_2}{P_1} = \frac{2500 \times 2499}{3001 \times 501} \qquad \ldots(iii)$$

$$\frac{P_2}{P_1} = 4{\cdot}157 \qquad \ldots(iv)$$

$$\approx 4{\cdot}2$$

It means the transfer of one particle from the middle to the upper and one particle from the middle to the lower state has changed the probability by a factor 4·2. This shows that both these distributions are not near the equilibrium state.

9·5 Maxwell-Boltzmann Distribution in terms of Temperature

The total energy of an isolated system is given by

$$U = \sum_i n_i E_i$$

$$U = n_1 E_1 + n_2 E_2 + n_3 E_3 + \ldots\ldots$$

$$U = \left(g_1 e^{-\alpha - \beta E_1}\right) E_1 + \left(g_2 e^{-\alpha - \beta E_2}\right) E_2 + \ldots\ldots$$

$$U = e^{-\alpha}\left[g_1 E_1 e^{-\beta E_1} + g_2 E_2 e^{-\beta E_2} + \ldots\ldots\right]$$

But $$e^{-\alpha} = \frac{N}{Z}$$

$$\therefore \quad U = \frac{N}{Z}\left[g_1 E_1 e^{-\beta E_1} + g_2 E_2 e^{-\beta E_2} + \ldots\ldots\right]$$

$$U = \frac{N}{Z}\sum_i g_i E_i e^{-\beta E_i} \qquad \ldots(i)$$

Here $$Z = \sum_i g_i e^{-\beta E_i}$$

$$\frac{dZ}{d\beta} = \frac{d}{d\beta}\sum_i g_i e^{-\beta E_i} = -\sum_i g_i E_i e^{-\beta E_i}$$

$$\therefore \quad \sum g_i E_i e^{-\beta E_i} = -\frac{d}{d\beta}\sum_i g_i e^{-\beta E_i}$$

Substituting this value in equation (i)

$$U = -\frac{N}{Z}\frac{d}{d\beta}\sum_i g_i e^{-\beta E_i}$$

$$U = -\frac{N}{Z}\frac{dZ}{d\beta}$$

$$U = -N\frac{d}{d\beta}\left[\log_e Z\right] \qquad \ldots(ii)$$

The average energy of a particle is

$$E_{av} = \frac{U}{N} = -\frac{d}{d\beta}\left(\log_e Z\right) \qquad \ldots(iii)$$

This shows that for a given system, the total energy U, the partition function Z, and the average energy of the particle E_{av}, depend on the parameter β. Therefore, β may be taken to characterise the internal energy of the system and has the units per joule. If T is the temperature in degrees kelvin, then it is more convenient to represent parameter β as

$$\beta = \frac{1}{kT} \quad \text{or} \quad kT = \frac{1}{\beta} \qquad \ldots(iv)$$

Here kT has the unit of energy *i.e.* joule and k is the Boltzmann's constant. Its units are J/K. The value of k is given by

$$k = 1{\cdot}3805 \times 10^{-23}\ \text{J/K}$$

Substituting the value of

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

in all the equations, we get

$$Z = \sum_i g_i\, e^{-(E_i/kT)} \qquad \ldots(v)$$

$$n_i = \frac{N}{Z} g_i\, e^{-(E_i/kT)} \qquad \ldots(vi)$$

This equation represents the Maxwell-Boltzmann distribution law in terms of the temperature of the system.

As $\beta = \dfrac{1}{kT}$

$$d\beta = -\frac{dT}{kT^2}$$

Substituting this value in equation (*ii*)

$$\therefore \quad U = \left(k N T^2\right)\frac{d}{dT}\left(\log_e Z\right) \qquad \ldots(vii)$$

Also, from equation (*iii*)

$$E_{av} = \left(kT^2\right)\frac{d}{dT}\left(\log_e Z\right) \qquad \ldots(viii)$$

Equation (*viii*) gives the relation between the average energy of the particle and its temperature under equilibrium position. Hence, the temperature of a system in statistical equilibrium is the

physical quantity related to the average energy of the particle of the system.

9·6 Maxwell's-Boltzmann Distribution and Ideal Gas

Most of the gases obey Maxwell-Boltzmann distribution over a wide range of temperature. Consider a gas having mono-atomic molecules. It is assumed that the gas is ideal and has only kinetic energy of translation. Inter-molecular attraction is assumed to be absent. If the kinetic energy is not quantized but considered to possess continuous values of energy, then the partition function Z can be written as

$$Z = \int_0^\infty e^{-(E/kT)}\, g(E)\, dE$$

Here g_i is replaced by $g\,(E)\,dE$

But $$g\,(E)\,dE = \left(\frac{4\pi V\,(2\ m^3)^{\frac{1}{2}}}{h^3}\right) E^{\frac{1}{2}}\ dE$$

Here V is the volume occupied by the gas and h is Planck's constant.

$$\therefore \quad Z = \frac{4\pi V\,(2m^3)^{\frac{1}{2}}}{h^3}\int_0^\infty E^{\frac{1}{2}}\ e^{-(E/kT)}\, dE$$

$$Z = \frac{4\pi V\,(2m^3)^{\frac{1}{2}}}{h^3}\left[\frac{\sqrt{\pi}(kT)^3}{2}\right]$$

$$Z = \frac{V(2\pi\, m\, k\, T)^{3/2}}{h^3} \qquad \ldots(i)$$

Equation (*i*) represents the partition function for an ideal mono-atomic gas in terms of the volume and temperature of the gas.

Taking logarithms on both sides

$$\log_e Z = \log_e\left[\frac{(2\pi m)^{3/2}\, V}{h^3}\right] + \log_e (kT)^{3/2}$$

$$\log_e Z = C + \frac{3}{2}\log_e kT \qquad \ldots(ii)$$

Also

$$E_{av} = (kT^2)\frac{d}{dT}(\log_e Z)$$

$$E_{av} = kT^2\frac{d}{dT}\left[C + \frac{3}{2}\log_e kT\right]$$

$$= kT^2\frac{d}{dT}\left[C + \frac{3}{2}\log_e k + \frac{3}{2}\log_e T\right]$$

$$E_{av} = \frac{3}{2}kT \qquad \ldots(iii)$$

The total energy,

$$U = N\, E_{av}$$

$$U = N\left(\frac{3}{2}\ kT\right)$$

$$U = \frac{3}{2}\ NkT \qquad \ldots(iv)$$

Equation (*iv*) shows that the internal energy of an ideal mono-atomic gas depends only on its temperature. The same relation does not however, hold good for real gases. In the case of real gases the internal energy is partly potential and partly kinetic. The total energy depends on the volume of the gas.

9·7 Quantum Statistics

In Maxwell-Boltzmann distribution, it has been assumed that all the energy levels are accessible to all the particles of the system. However, there may be certain levels prohibited to a certain group of particles. Each energy state is associated with a certain available wave function. The probability of a particular distribution is restricted by the available wave functions of any state. These restrictions are taken into account in quantum statistics. There are two types of quantum statistics

(*i*) Fermi-Dirac statistics

(*ii*) Bose-Einstein statistics.

In Fermi-Dirac statistics the particles are assumed to obey Pauli's exclusion principle. They are characterised by antisymmetric wave functions. The particles under this category are called ***fermions***. Protons ,neutrons and electrons are fermions.

In the case of Bose-Einstein statistics, it is assumed that the particles are not restricted by Pauli's exclusion principle and are characterised by symmetric wave functions. These particles are called ***bosons***. It has been experimentally found that all particles having spin zero or integral multiple of 1 are bosons. Helium nuclei and mesons are bosons.

In both the kinds of quantum statistics, the particles are identical and indistinguishable. At high temperature and low pressure, all the three statistics give practically the same result.

9·8 Phase Space

From the statistical point of view, a mono-atomic gas constitutes the simplest system. The state of the gas is completely known if the position and momentum of each atom of the gas is specified. The position of an atom can be specified in terms of its rectangular coordinates, x, y and z. The momentum of an atom is completely known if its rectangular components p_x, p_y and p_z are specified. These six quantities x, y, z, p_x, p_y, p_z for each atom when known, the state of the gas can be determined.

The three rectangular coordinates x, y, z describing the position of an atom and the three rectangular components of momentum

of the atom p_x, p_y, p_z together give the state of an atom in a six-dimensional space called the *phase-space*.

The phase space can be further sub-divided into small elements of sides $\triangle x$, $\triangle y$, $\triangle z$, $\triangle p_x$, $\triangle p_y$, $\triangle p_z$.

The volume of each state is given by

$$H = \triangle x\ \triangle y\ \triangle z\ \triangle p_x\ \triangle p_y\ \triangle p_z \qquad \ldots(i)$$

According to Hiesenburg's uncertainty principle,

$$\triangle x\ \triangle p_x \approx h$$

$$\triangle y\ \triangle p_y \approx h$$

$$\triangle z\ \triangle p_z \approx h$$

$$\therefore\ \triangle x\ \triangle p_x\ \triangle y\ \triangle p_y\ \triangle z\ \triangle p_z = h^3 \qquad \ldots(ii)$$

Comparing (*i*) and (*ii*),

Volume of each state is given by

$$H = h^3 \qquad \ldots(iii)$$

Therefore, according to uncertainty principle, in phase space, the coordinates of a particle can be specified only to the extent that the particle under consideration has the position and momentum lying within an element of phase space of volume h^3. The unit of phase space volume is

$$(\text{joule—s})^3$$

9·9 Fermi-Dirac Distribution Law

Consider a system consisting of a large number of particles. It is assumed (*i*) that the particles are ***identical*** and ***indistinguishable*** and (*ii*) that the particles obey exclusion principle. It means that no two particles can have the same dynamical state and the wave function of the whole system must be antisymmetric. The particle satisfying these conditions are called *fermions*. In general, all fundamental particles with spin $\frac{1}{2}$ are fermions.

In quantum statistics the intrinsic probability g_i is governed by the different quantum states relating to a given energy *i.e.* the degeneracy of the energy state. Each quantum state corresponds to a particle wave function. The wave functions are determined by each of the possible arrangements of quantum number corresponding to a given energy level. For particles with spin $\frac{1}{2}$, in the absence of magnetic forces, each of the particle may be in the energy states with spin $+\frac{1}{2}$ or $-\frac{1}{2}$. Hence the intrinsic probability g_i in this case is 2. For motion in a central field, the energy of the particle is independent of the orientation of the orbital angular momentum. Due to this, a degeneracy of $(2l+1)$ is introduced and it is the value of g for that particular energy state. If the particles possess spin, the total degeneracy $= 2\ (2l+1)$. As no two particles can be in the same energy state having the same quantum number, the intrinsic probabilities g_i's give the maximum number of particles that can be accommodated in a particular energy level without violating the exclusion principle *i.e.*

$$n_i \leqslant g_i$$

It means that the n_i value for a given distribution does not exceed the corresponding value of g_i.

Let n_i be the number of particles for energy level E_i. The first particle can be placed in any one of the available g_i states *i.e.* this particle can be assigned to any of the g_i sets of quantum numbers. Thus, the first particle can be distributed in g_i different ways. Similarly, the second particle can be arranged in (g_i-1) different ways and the process continues.

Thus, the total number of different ways of arranging n_i particles among the available g_i states with energy level E_i is

$$= g_i\,(g_i-1)\,(g_i-2).....[g_i-(n_i-1)]$$

$$= \frac{g_i\,!}{(g_i-n_i)\,!} \qquad ...(i)$$

Further, if the particles are taken to be indistinguishable, it will not be possible to detect any difference when n_i particles are reshuffled into different states occupied by them in the energy level E_i. Therefore, the total number of different and distinguishable ways is,

$$= \frac{g_i\,!}{n_i\,!\,(g_i-n_i)\,!} \qquad ...(ii)$$

Therefore, the total number of different and distinguishable ways of getting the distribution n_1, n_2, n_3, *etc.*, among the various energy levels, E_1, E_2, E_3...etc. can be obtained by multiplying the various factors.

$$\therefore \quad P = \frac{g_1\,!}{n_1\,!\,(g_1-n_1)\,!}\cdot\frac{g_2\,!}{n_2\,!\,(g_2-n_2)\,!}.....$$

$$P = \prod_i \frac{g_i\,!}{n_i\,!\,(g_i-n_i)\,!} \qquad ...(iii)$$

The most probable distribution can by obtained by evaluating the maximum value of $\log_e P$ in equation (*iii*).

This should also satisfy the condition that

$$\sum_i n_i = N \text{ and } \sum_i n_i E_i = U.$$

According to Stirling's approximation,

$$\log_e x\,! = x\log_e x - x$$

From equation (*iii*), applying Striling's approximation,

$$\log_e P = \sum_i [(g_i\log_e g_i - g_i) - (n_i\log_e n_i - n_i) - [(g_i-n_i)\log_e (g_i-n_i) - (g_i-n_i)]$$

$$\log_e P = \sum_i [g_i\log_e g_i - n_i\log_e n_i - (g_i-n_i)\log_e (g_i-n_i)] \qquad ...(iv)$$

Differentiating equation (*iv*)

$$-d\,(\log_e P) = \sum_i [\log_e n_i - \log_e (g_i-n_i)]\,dn_i$$

To obtain the maximum value of P,

$$d\,(\log_e P) = 0$$

$$\therefore \quad \sum_i [\log_e n_i - \log_e (g_i-n_i)]\,dn_i = 0 \qquad ...(v)$$

But $$\sum_i dn_i = 0 \qquad ...(vi)$$

and $$\sum_i E_i\,dn_i = 0 \qquad ...(vii)$$

Multiplying (*vi*) by α and (*vii*) by β and adding to equation (*v*), we get

$$\sum_i [\log n_i - \log_e (g_i-n_i) + \alpha + \beta E_i]\,dn_i = 0$$

The equilibrium distribution is possible if

$$\therefore \quad \log_e n_i - \log_e (g_i-n_i) + \alpha + \beta E_i = 0 \qquad ...(viii)$$

$$\log_e\left(\frac{n_i}{g_i-n_i}\right) = -\alpha-\beta E_i$$

or $$\frac{n_i}{g_i-n_i} = e^{-\alpha-\beta E_i}$$

or $$\frac{g_i-n_i}{n_i} = e^{\alpha+\beta E_i}$$

$$\frac{g_i}{n_i} - 1 = e^{\alpha+\beta E_i}$$

or $$\frac{g_i}{n_i} = \left(e^{\alpha+\beta E_i}\right)+1$$

or $$n_i = \frac{g_i}{\left(e^{\alpha+\beta E_i}\right)+1} \qquad ...(ix)$$

Equation (*ix*) represents the Fermi-Dirac distribution law. The parameter has the same role as in the case of Maxwell-Boltzmann distribution law *i.e.* for the system consisting of fermions in statistical equilibrium.

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

$$\therefore \quad n_i = \frac{g_i}{[e^{(\alpha+E_i/kT)}]+1} \qquad ...$$

In most cases the value of α is negative and is taken to be equal to

$$\frac{-E_F}{kT}$$

$$\therefore \quad n_i = \frac{g_i}{\left[e^{(E_i-E_F)/kT}\right]+1} \qquad ...(xi)$$

The value of E_F is positive and is independent of temperature.

For $T = 0$, all the energy states are fully occupied and $n_i = g_i$. All the states with $E > E_F$, are empty *i.e.* $n_i = 0$.

$$\left[\ e^{(E_i - E_F)/kT}\right] = \begin{cases} 0 \text{ for } E_i - E_F < 0 \\ \infty \text{ for } E_i - E_F > 0 \end{cases}$$

Limit $T \to 0$

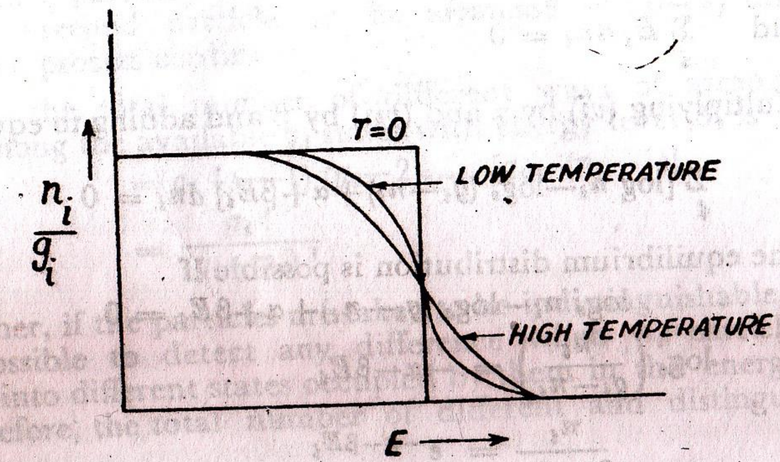


Fig. 9·2

In the case of Fermi-Dirac statistics, the accumulation of particles at the ground level is not allowed and at temperature $T = 0$, the particles occupy the lowest energy levels upto E_F. Here, the energy E_F gives the indication of the maximum energy of the fermions in the system. E_F is also called Fermi energy. For higher temperatures, the particles occupy higher energy states greater than E_F. The curves (Fig. 9·2) indicate that only those fermions with energies close to E_F can move into unoccupied higher energy states. If $k\theta_F = E_F$, the temperature θ_F is called the Fermi temperature.

9·10 Electron Gas

Electrons in a metal belong to a most characteristic system of fermions because electrons obey the exclusion principle. For electrons in a metal, the energy levels are grouped in bands. Practically at all temperatures, the lower level energy bands are filled with electrons. The upper level energy bands are only partially filled with electrons. The distribution of electrons is to be considered only in the upper bands called the conduction band. The zero energy level is taken at the lowest level of the conduction band. It is also assumed that the electrons have free movement within the conductor, provided the energy associated with the electrons is of the order of upper level energy bands. As the energy of the electron in the conduction band is continuous, the term g_i is replaced by $g\,(E)\,dE$. Here dn electrons have energy in the range E and $E+dE$. According to Fermi-Dirac distribution law

$$n_i = \frac{g_i}{\left[\ e^{(E_i - E_F)/kT}\right] + 1} \qquad \ldots(i)$$

Substituting the value of $g_i = g\,(E)\,dE$ in equation (*i*) and replacing n_i by dn

$$dn = \frac{g\,(E)\,dE}{\left[\ e^{(E_i - E_F)/kT}\right] + 1}$$

As an electron has the spin $\pm \frac{1}{2}$, the total number of states in the sphere is twice. $V/(2\pi)^3$ refers to the translational states per unit volume in the Fermi space Fermi sphere of radius k_F has the total number of particles accomodated,

$$n = \frac{2\left[\frac{V}{(2\pi)^3}\right]\left(\frac{4}{3}\ \pi (k_F)^3\right)}{\left[\ e^{(E_i - E_F)/kT}\right] + 1}$$

Here $$E = \frac{p^2}{2m} = \frac{\left(\frac{h}{2\pi}\right)^2 (k_F)^2}{2m}$$

$$\therefore \quad k_F = \frac{p}{h/2\pi} = \frac{2\pi p}{h}$$

$$\therefore \quad n = \frac{2\left[\frac{V}{(2\pi)^3}\right]\left[\frac{4}{3}\pi \left(\frac{2\pi p}{h}\right)^3\right]}{\left[\ e^{(E_i - E_F)/kT}\right] + 1}$$

But $p = (2mE)^{1/2}$

$$\therefore \quad n = \frac{2\left[\frac{V}{(2\pi)^3}\right]\left[\frac{4}{3}\pi \left(\frac{2\pi}{h}\right)^3 (2mE)^{3/2}\right]}{\left[\ e^{(E_i - E_F)/kT}\right] + 1}$$

$$n = \frac{\left(\frac{8\pi V}{3h^3}\right)(2m)\,(2m)^{1/2}\,E^{3/2}}{\left[\ e^{(E_i - E_F)/kT}\right] + 1}$$

Differentiating

$$dn = \frac{\left(\frac{8\pi V}{3h^3}\right)(2m)\,(2m)^{1/2} \times \frac{3}{2}\,E^{1/2}\,dE}{\left[\ e^{(E_i - E_F)/kT}\right] + 1}$$

$$\frac{dn}{dE} = \frac{\left[\frac{8\pi V\,(2m^3)^{1/2}}{h^3}\right]E^{1/2}}{\left(\ e^{(E_i - E_F)/kT}\right) + 1} \qquad \ldots(ii)$$

Equation (*ii*) represents the energy distribution for free electrons. This is also called Fermi-Dirac formula of free fermions.

At $T = 0$K,

$$p = (2m\,E_F)^{1/2} \qquad \ldots(iii)$$

and $$N = \left(\frac{2V}{h^3}\right)\left(\frac{4}{3}\ \pi p^3\right)$$

or $$p = \left(\frac{3Nh^3}{8\pi V}\right)^{1/3} \qquad ...(iv)$$

Equating (*iii*) and (*iv*)

$$(2mE_F)^{1/2} = \left(\frac{3Nh^3}{8\pi V}\right)^{1/3}$$

Squaring

$$2mE_F = \left(\frac{3Nh^3}{8\pi V}\right)^{2/3}$$

or $$E_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad ...(v)$$

Knowing the value of $\frac{N}{V}$ *i.e.* the number of free electrons per unit volume, the Fermi energy for electrons in a metal can be obtained.

For silver, the value $\frac{N}{V} = 5{\cdot}86\times10^{28}$ electrons/m^3

$$\therefore \quad E_F = \left(\frac{(6{\cdot}624\times10^{-34})^2}{8\times9\times10^{-31}}\right)\left(\frac{3\times5{\cdot}86\times10^{28}}{3{\cdot}14}\right)^{2/3}$$

$$E_F = 9\times10^{-19}\ \text{J}$$

But $1\ \text{eV} = 1{\cdot}6\times10^{-19}$ J

$$\therefore \quad E_F = \frac{9\times10^{-19}}{1{\cdot}6\times10^{-19}}$$

$$E_F = 5{\cdot}625\ \text{eV}$$

It means that the maximum kinetic energy of free electrons in silver at absolute zero temperature is 5·6 eV.

The Fermi temperature θ_F is given by

$$\theta_F = \frac{E_F}{k}$$

As E_F is practically independent of temperature, the value θ_F is fixed for a given metal. The values of θ_F and E_F are given in the following table.

TABLE

Metals	E_F *(electron volts)*	θ_F (K)
Potassium	2·14	$2{\cdot}4\times10^4$
Sodium	3·12	$3{\cdot}7\times10^4$
Lithium	4·72	$5{\cdot}5\times10^4$
Silver	5·51	$6{\cdot}4\times10^4$
Gold	5·54	$6{\cdot}4\times10^4$
Copper	7·04	$8{\cdot}2\times10^4$

9·11 Bose-Einstein Distribution Law

Bose-Einstein distribution is applied to systems composed of identical and indistinguishable particles that are not restricted by the exclusion principle. In such systems, there is no limit to the number of particles occupying a particular quantum state. These particles are called *bosons*. Their spin is zero or 1. Mesons and helium nuclei are examples of bosons.

In the case of Bose-Einstein statistics the values of g_i refer to degeneracy of each energy level. Suppose, that n_i particles are arranged in a row and distributed among g_i quantum states with (g_i-1) partitions in between. The total number of possible arrangements of particles and partitions is equal to the total number of permutations of (n_i+g_i-1) objects in a row. Therefore the total possible ways of arranging n_i particles with g_i-1 partitions

$$= (n_i+g_i-1)\,!$$

As the particles are identical and indistinguishable the possible number of distinct arrangements

$$= \frac{(n_i+g_i-1)\,!}{n_i\,!\,(g_i-1)\,!}$$

The total number of distingiushable and distinct ways of arranging N particles in all the available energy states is given by

$$P = \frac{(n_1+g_1-1)\,!}{n_1\,!\,(g_1-1)\,!} \times \frac{(n_2+g_2-1)\,!}{n_2\,!\,(g_2-1)\,!} \times \ldots\ldots$$

$$P = \prod_i \frac{(n_i+g_i-1)\,!}{n_i\,!\,(g_i-1)\,!} \qquad ...(i)$$

The most probable distribution can be obtained by finding the maximum value of $\log_e P$.

According to Stirling's approximation

$$\log_e x\,! = x\log_e x - x$$

Also $$\sum_i n_i = N \qquad ...(ii)$$

and $$\sum_i n_i E_i = U \qquad ...(iii)$$

From equation (*i*), applying Stirling's approximation

$$\log_e P = \sum_i [\log_e (n_i+g_i-1)\,! - \log_e n_i\,! - \log_e (g_i-1)\,!]$$

$$\log_e P = \sum_i [(n_i+g_i-1)\log_e (n_i+g_i-1) - (n_i+g_i-1) - (n_i\log_e n_i - n_i) - [(g_i-1)\log_e (g_i-1) - (g_i-1)]$$

$$\log_e P = \sum_i [(n_i+g_i-1)\log_e (n_i+g_i-1) - n_i\log_e n_i - (g_i-1)\log_e (g_i-1)] \qquad ...(iv)$$

The maximum value of P is obtained by taking $d\ (\log_e P) = 0$

Differentiating equation P.

$$d\ (\log_e P) = \sum_i [\log_e (n_i+g_i-1)\ dn_i - \log_e n_i\ dn_i] = 0$$

$$\therefore \quad -d\ (\log_e P) = \sum_i [-\log_e (n_i+g_i-1)\ dn_i + \log_e n_i dn_i] = 0$$

or
$$\sum_i [-\log_e (n_i+g_i-1)+\log_e n_i]\ dn_i = 0 \qquad ...(v)$$

As the total number of particles and total energy are constants, we have,

$$\sum_i dn_i = 0 \qquad ...(vi)$$

$$\sum_i E_i\ dn_i = 0 \qquad ...(vii)$$

Multiplying equation (vi) by α and equation (vii) by β and adding to equation (v) we get,

$$\sum_i [-\log_e (n_i+g_i-1)+\log_e n_i+\alpha+\beta E_i]\ dn_i = 0$$

$$\therefore \quad -\log_e (n_i+g_i-1)+\log_e n_i+\alpha+\beta E_i = 0$$

Taking n_i+g_i very large as compared to 1, the quantity 1 can be neglected.

$$\therefore \quad -\log_e (n_i+g_i)+\log_e n_i+\alpha+\beta E_i = 0$$

$$\log_e \left(\frac{n_i}{n_i+g_i}\right) = -\alpha-\beta E_i$$

$$\frac{n_i}{n_i+g_i} = e^{-\alpha-\beta E_i}$$

or
$$\frac{n_i+g_i}{n_i} = e^{\alpha+\beta E_i}$$

or
$$1+\frac{g_i}{n_i} = e^{\alpha+\beta E_i}$$

$$\frac{g_i}{n_i} = \left(e^{\alpha+\beta E_i}\right)-1$$

or
$$n_i = \frac{g_i}{\left(e^{\alpha+\beta E_i}\right)-1} \qquad ...(viii)$$

Equation $(viii)$ refers to Bose-Einstein distribution law.

Taking $\beta = \frac{1}{kT}$

$$n_i = \frac{g_i}{\left[e^{(\alpha+E_i/kT)}\right]-1} \qquad ...(ix)$$

The value of the constant α is governed by the equation $\Sigma n_i = N$. As n_i cannot be negative, α must always have a positive value. The distribution of the particles for different energy levels is shown in Fig. 9·3 for low and high temperatures.

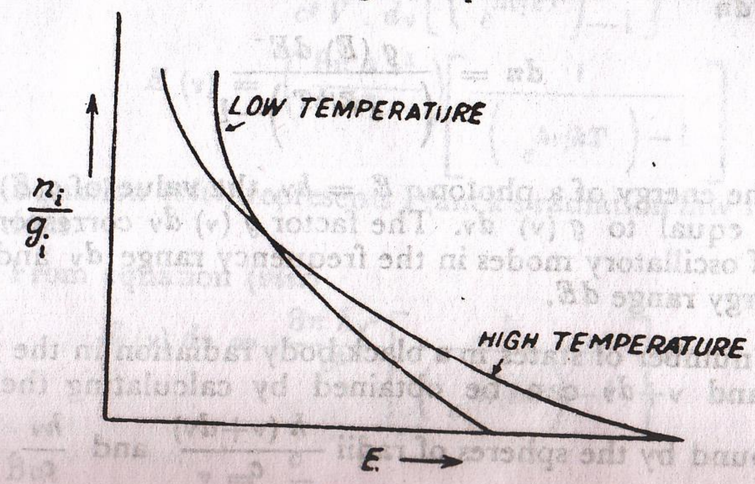


Fig. 9·3

The Bose-Einstein distribution has more emphasis on the lower energy levels.

9·12 Photon Gas

The interaction of electromagnetic radiations with matter, led to the idea that electromagnetic radiations are composed of discrete energy particles called *photons*. Each photon has an energy $h\nu$ and momentum $\frac{h}{\lambda}$. Here ν is the frequency and λ is the wavelength of the radiations. The electromagnetic radiations trapped in a cavity and in thermal equilibrium with the walls of the cavity are termed as black body radiations. In the equilibrium condition, the black body radiations can be considered as the ***photon gas***. It is assumed that the photons do not interact among themselves. The photons interact only with the atoms of the walls of the cavity. It is further assumed that the photons are indistinguishable and many photons can have the same energy. Photons are taken as bosons and they obey Bose-Einstein statistics.

As the photons can either be emitted or absorbed by the atoms of the walls of the cavity, the number of photons is not constant *i.e.* the condition $\sum_i dn_i = 0$ is no longer valid.

Due to this reason the value of α is equal to zero in the Bose-Einstein distribution law.

$$n_i = \frac{g_i}{\left(e^{(\alpha+E_i/kT)}\right)-1} \qquad ...(i)$$

Here $\alpha = 0$

$$\therefore \quad n_i = \frac{g_i}{\left(e^{E_i/kT}\right)-1} \qquad ...(ii)$$

In case, the cavity is large as compared to the wavelength of the radiations, the energy spectrum of the photons is taken to be continuous. In this case, the energy difference between successive allowed energy values is very small. Thus, replacing g_i by $g(E)\,dE$, and n_i by dn

$$dn = \frac{g\,(E)\,dE}{\left(e^{E/kT}\right)-1} \qquad \ldots(iii)$$

As the energy of a photon, $E = h\nu$, the value of $g(E)\,dE$ can be taken equal to $g\,(\nu)\,d\nu$. The factor $g\,(\nu)\,d\nu$ corresponds to the number of oscillatory modes in the frequency range $d\nu$ and relating to the energy range dE.

The number of states in a black body radiation in the frequency range ν and $\nu+d\nu$ can be obtained by calculating the spherical volume bound by the spheres of radii $\frac{h\,(\nu+d\nu)}{c}$ and $\frac{h\nu}{c}$.

The volume of the spherical shell

$$= \frac{4}{3}\,\pi\,\frac{h^3}{c^3}\,(\nu+d\nu)^3 - \frac{4}{3}\,\pi\,\frac{h^3}{c^3}\,\nu^3$$

$$= \frac{4}{3}\,\pi\,\frac{h^3}{c^3}\left[\,\nu^3+3\nu^2 d\nu+\ldots-\nu^3\,\right]$$

$$= \frac{4}{3}\,\pi\,\frac{h^3}{c^3}\times 3\nu^2 d\nu$$

$$= 4\pi\,\frac{h^3}{c^3}\,\nu^2\,d\nu \qquad \ldots(iv)$$

The phase space has volume $V = h^3$ and there are two states of polarization for the radiation. The number of states in the black body radiation in the frequency range ν and $\nu+d\nu$ is given by

$$g\,(\nu)\,d\nu = \frac{8\pi\,\nu}{c^3}\,\nu^2\,d\nu \qquad \ldots(v)$$

$$\therefore \quad dn = \left(\frac{8\pi\,V\,\nu^2 d\nu}{c^3}\right)\frac{1}{\left(e^{h\nu/kT}\right)-1} \qquad \ldots(vi)$$

For dn photons in the frequency range $\nu+d\nu$ and ν, the energy is equal to $(h\nu)\,dn$ and the energy per unit volume

$$= \frac{(h\nu)\,dn}{\nu}$$

Therefore, the energy density distribution for black body radiation is given by

$$E\,(\nu) = \frac{(h\nu)\,dn}{V\,.\,d\nu} \qquad \ldots(vii)$$

Substituting the value of dn from equation (vi), we get

$$E\,(\nu) = -\frac{8\pi\,V\,\nu^2\,d\nu\,.\,h\nu}{c^3\,V\,.\,d\nu\left[\left(e^{h\nu/kT}\right)-1\right]}.$$

$$E\,(\nu) = \left(\frac{8\pi\,h\,\nu^3}{c^3}\right)\left[\frac{1}{\left(e^{h\nu/kT}\right)-1}\right] \qquad \ldots(vii)$$

Equation $(viii)$ represents Planck's radiation law for black body radiations.

From equation $(viii)$

$$E\,(\nu)\,d\nu = \frac{8\pi\,h\nu^3}{c^3}\left[\frac{1}{\left(e^{h\nu/kE}\right)-1}\right]d\nu$$

But $$\nu = \frac{c}{\lambda}$$

or $$d\nu = -\frac{c}{\lambda^2}\,d\lambda$$

Neglecting the negative sign, we get

$$\therefore \quad E\,(\lambda)\,d\lambda = \frac{8\pi\,h\nu^3}{c^3}\times\frac{c}{\lambda^2}\left[\frac{1}{\left(e^{h\nu/kT}\right)-1}\right]d\lambda$$

or $$E\,(\lambda) = \frac{8\pi\,hc}{\lambda^5}\left[\frac{1}{\left(e^{h\nu/kT}\right)-1}\right] \qquad \ldots(ix)$$

This gives the energy density for wavelength λ in the spectrum of the black body. Both the equations $(viii)$ and (ix) represent Planck's radiation law for black body radiation.

9·13 Comparison of the Three Statistics

Maxwell-Boltzmann	*Fermi-Dirac*	*Bose-Einstein*
1. Particles are distinguishable.	1. Particles are indistinguishable.	1. Particles are indistinguishable.
2. Only particles are taken into consideration.	2. Only quantum states are taken into consideration.	2. Only quantum states are taken into consideration.
3. There is no restriction on the number of particles in a given state.	3. There is restriction on the number of particles in a given quantum state.	3. There is no restriction on the number of particles in a given quantum state.
4. Volume of the state in six dimensional space is not known.	4. Phase space is known $V = h^3$	4. Phase space is known $V = h^3$

Maxwell-Boltzmann	*Fermi-Dirac*	*Bose-Einstein*
5. Number of distinguishable ways are given by $P = \prod_i^N \frac{g_i^{n_i}}{n_i!}$.	5. Number of distinguishable ways are given by $P = \prod_i \frac{g_i!}{n_i!(g_i - n_i)}$	5. Number of distinguishable ways are given by $P = \prod_i \frac{(n_i + g_i - 1)!}{n_i!\,(g_i - 1)!}$
6. Maximum probability distribution $\propto \frac{1}{e^{(\alpha+\beta E_i)}}$	6. Maximum probability distribution $\propto \frac{1}{[\,e^{(\alpha+\beta E_i)}+1]}$	6. Maximum probability distribution $\propto \frac{1}{[\,e^{(\alpha+\beta E_i)}\,]-1}$
7. —	7. At high temperatures, Fermi-Dirac distribution approaches Maxwell-Boltzmann distribution.	7. At high temparatures Bose-Einstein distribution approaches Maxwell-Boltzmann distribution.
8. Applicable to ideal gas molecules	8. Applicable to electrons of high concentration.	8. Applicable to photons and symmetrical particles such as a particles.
9. Internal energy of an ideal monoatomic gas depends only on its temperature. At absolute zero, energy is zero.	9. Due to Pauli's exclusion principle, all the electrons cannot occupy the lowest energy level. Even at absolute zero temperature, some of the electrons are distributed at higher energy levels. Hence, at absolute zero, the energy is not zero. Therefore, at the complete degenerate state, the energy is independent of temperature.	9. The energy at absolute zero is taken to be zero.
10. $n_i = \frac{g_i}{e^{(\alpha+\beta E_i)}}$	10. $n_i = \frac{g_i}{[\,e^{(\alpha+\beta E_i)}+1\,]}$	10. $n_i = \frac{g_i}{[\,e^{(\alpha+\beta E_i)}-1\,]}$

11. All the three distributions can be represented by a single equation

$$\frac{g_i}{n_i} = [\,e^{(\alpha+\beta E_i)} + \delta]$$

Here $\delta = 0$ Here $\delta = +1$ Here $\delta = -1$

If $\frac{g_i}{n_i} \gg 1$ or $n_i \ll g_i$, i.e. δ can be neglected. In the case of diluted systems, the three statistics lead practically to similar results. It means that at high temperatures, the three statistics give practically the same results.

Example 9·2 *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) Fermi-Dirac and (iii) Bose-Einstein statistics.*

(1) Maxwell Boltzmann statistics

In this case, the particles are distinguishable and there is no limit to the number of particles in any one state. The total number of ways is $3^2 = 9$

States	*Possible Distribution in various States*								
1	*a*	*b*	—	—	*a*	*b*	*a b*	—	—
2	*b*	*a*	*a*	*b*	—	—	—	*a b*	—
3	—	—	*a*	*a*	*b*	*a*	—	—	*a b*

2. Fermi-Dirac statistics

In this case, the particles are indistinguishable and not more than one particle can be in any one state. Here $a = 0$ The total number of ways = 3.

States	*Possible distribution in various states*		
1	*a*	*a*	—
2	*a*	—	*a*
3	—	*a*	*a*

(3) Bose-Einstein statistics

In this case, the particles are indistinguishable and there is no limit to the number of particles in any one state. Here $a = b$. The total number of ways = 6

States	*Possible Distribution in various states*					
1	*a*	*a*	—	*aa*	—	—
2	*a*	—	*a*	—	*aa*	—
3	—	*a*	*a*	—	—	*aa*

Exercises IX

1. Distinguish between classical and quantum statistics.

2. Explain what you understand by the term statistical equilibrium ?.

3. Discuss Maxwell-Boltzmann distribution law and derive the relation.

$$n_i = g\, e^{(-\alpha-\beta E_i)}$$

4. On the basis of Maxwell—Boltzmann statistics show that the temperature of a system in statistical equilibrium is related to average energy of the particles of the system.

5. Applying Maxwell-Boltzmann distribution law, show that the internal energy of an ideal mono-atomic gas depends only on its temperature.

6. Discuss-Fermi-Dirac distribution law and show that

$$n_i = \frac{g_i}{[e^{(\alpha+\beta E_i)}]+1}$$

7. Applying Fermi-Dirac distribution to an electron gas, show that

$$E_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3}$$

8. Discuss Bose-Einstein distribution law and derive the equation

$$n_i = \frac{g_i}{[e^{(\alpha+\beta E_i)}]-1}$$

9. Apply Bose-Einstein distribution law to a photon gas.

10. From Bose-Einstein statistical thermodynamics show that

$$E(\lambda) = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{\left(e^{hv/kT}\right)-1}\right]$$

11. Derive Planck's radiation law for the black body radiation.

12. Distinguish between (*i*) Maxwell-Boltzmann (*ii*) Fermi-Dirac and (*iii*) Bose-Einstein statistics. Give examples.

13. Establish the distribution law of Maxwell and Boltzmann. [*Delhi* (*Hons.*), *1978*]

14. Discuss the free electron gas model for metals. Obtain the distribution law for the electron gas in a metal at absolute zero. [*Delhi* (*Hons.*), *1978*]

15. Distinguish between Classical Statistics, Fermi-Dirac Statistics and Bose-Einstein Statistics. [*Delhi* (*Hons.*), *1978*]

16. Obtain an expression for Bose-Einstein distribution law. [*Delhi* (*Hons.*), *1978*]

17. Write short notes on :

(*i*) Statistical equilibrium

(*ii*) Electron gas

(*iii*) Photon gas

(*iv*) Phase space

(*v*) Quantum statistics

(*vi*) Fermi temperature

(*vii*) Fermi Energy

(*viii*) Planck's radiation law

(*ix*) Statistical thermodynamics

(*x*) Maxwell Boltzmann distribution law

(*xi*) Fermi-Dirac distribution law

(*xii*) Bose-Einstein distribution law

18. A system consists of 8000 particles distributed in three energy states with equal spacing. The energy of the three states are $E_1 = 0$, $E_2 = x$, $E_3 = 2x$. All the three states have the same intinsic probability g. At a certain instant, there are 4000 particles in the lower level, 3000 particles in the middle level and 1000 particles in the upper level. Compare the relative probabilities with the distribution obtained by the transfer of one particle from middle to the lower level and one particle from the middle to the upper level and the original distribution. [**Ans. 2·247**]

APPENDIX I

A-1 Variation of Surface Tension with Temperature

The surface tension of a liquid film decreases with increase in temperature. The variation of surface tension with temperature can be studied with the help of the first TdS equation

$$TdS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad ...(i)$$

In the case of a surface film, the corresponding TdS equation can be obtained by replacing V by A and P by $-S$

$$\therefore \quad TdS = C_A\,dT - T\left(\frac{\partial S}{\partial T}\right)_A dA \qquad ...(ii)$$

Here C_A represents the change in energy of a given surface film for one degree rise in temperature.

A represents the area of the film and S represents surface tension at temperature T.

Consider a very small drop of the liquid held in a metallic frame. Let the surface film of the drop be increased isothermally such that the final area of the film becomes A. If the surface tension of the film is a function of temperature only, then heat transferred

$$H = -T\left(\frac{dS}{dT}\right)(A-0)$$

or
$$H = -T\left(\frac{dS}{dT}\right)A \qquad ...(iii)$$

The work done

$$W = -S\,(A-0)$$

or
$$W = -SA \qquad ...(iv)$$

From the first law of thermodynamics

$$H = (U-U_0)+W$$

or
$$U-U_0 = H-W \qquad ...(v)$$

Substituting the values of H and W

$$U-U_0 = -T\left(\frac{dS}{dT}\right)A-(-SA)$$

$$U-U_0 = \left[S-T\left(\frac{dS}{dT}\right)\right]A \qquad ...(vi)$$

Here U_0 represents the energy of the liquid with practically no surface and U the energy of the liquid with a surface area A.

From equation (vi)

$$\left(\frac{U-U_0}{A}\right) = S-T\left(\frac{dS}{dT}\right) \qquad ...(vii)$$

Here $S-T\left(\frac{dS}{dT}\right)$ represents surface energy per unit area.

It represents that surface tension decreases with increase in temperature. It has been observed experimentally *that the surface tension becomes* zero at a critical temperature. For water, the critical temperature = 647 K.

For water at 647 K the heat of vaporization is also zero.

Table

Variation of Surface Tension of Water with Temperature

Temperature K	*Surface Tension* N/m
273	$7{\cdot}55\times10^{-2}$
373	$5{\cdot}15\times10^{-2}$
473	$2{\cdot}90\times10^{-2}$
573	$0{\cdot}96\times10^{-2}$
647	Zero

A-2 . Root Mean Square Velocity, Average Velocity and Most Probable Velocity

1. Root Mean Square Velocity

$$\frac{1}{2}\,m\,C_{rms}^2 = \frac{3}{2}\,kT$$

$$C_{rms}^2 = \frac{3kT}{m}$$

$$C_{rms} = \sqrt{\frac{3kT}{m}} \qquad ...(i)$$

2. Average Velocity

$$C_{ave} = \frac{\int_0^\infty C\, dN}{N}$$

But, according to Maxwell's law of distribution

$$dN = 4\pi N A^3 e^{-bc^2}\, c^2\, dC$$

$$\therefore \quad C_{ave} = \frac{\int_0^\infty C\, 4\pi N A^3\, e^{-bc^2}\, c^2\, dC}{N}$$

$$= 4\pi A^3 \int_0^\infty C^3\, e^{-bc^2}\, dC \quad = (4\pi A^3)\left(\frac{1}{2b^2}\right)$$

But $A = \left[\frac{m}{2\pi kT}\right]^{\frac{3}{2}}$ and $b = \frac{m}{2kT}$

$$\therefore \quad C_{ave} = \frac{4\pi}{2}\left[\frac{m}{2\pi kT}\right]^{3/2}\left(\frac{2kT}{m}\right)^2$$

$$C_{ave} = \left[\frac{8kT}{\pi m}\right]^{\frac{1}{2}} \qquad \ldots(ii)$$

3. Most Probable Velocity (C_m)

As C_m corresponds to the peak value, therefore, derivative of $\frac{dN}{dC}$ with respect to C should be zero.

$$\frac{d}{dC}\left[\frac{dN}{dC}\right] = \frac{d}{dC}\left[4\pi N A^3\, e^{-bc^2}\, C^2\right]_{C=C_m} = 0$$

$$4\pi N A^3 \frac{d}{dC}\left[e^{-bc^2}\, C^2\right]_{C=C_m} = 0$$

or

$$\frac{d}{dC}\left[e^{-bc^2}\, C^2\right]_{c=c_m} = 0$$

$$-2bC_m^2\, e^{-bc^2} + 2C_m e = 0$$

or

$$-bC_m^2 + 1 = 0$$

$$C_m = \left[\frac{1}{b}\right]^{\frac{1}{2}}$$

But $b = \frac{m}{2kT}$

$$C_m = \left[\frac{2kT}{m}\right]^{\frac{1}{2}} \qquad \ldots(iii)$$

$\therefore$ From equations (i), (ii) and (iii)

$$C_m : C_{ave} : C_{rms} = \left[\frac{2kT}{m}\right]^{\frac{1}{2}} : \left[\frac{8kT}{\pi m}\right]^{\frac{1}{2}} : \left[\frac{3kT}{m}\right]^{\frac{1}{2}}$$

$$= 1 : 1.128 : 1.224$$

This relation gives the relative magnitudes of the three velocities at a given temperature. The three velocities are shown in Fig. A-1

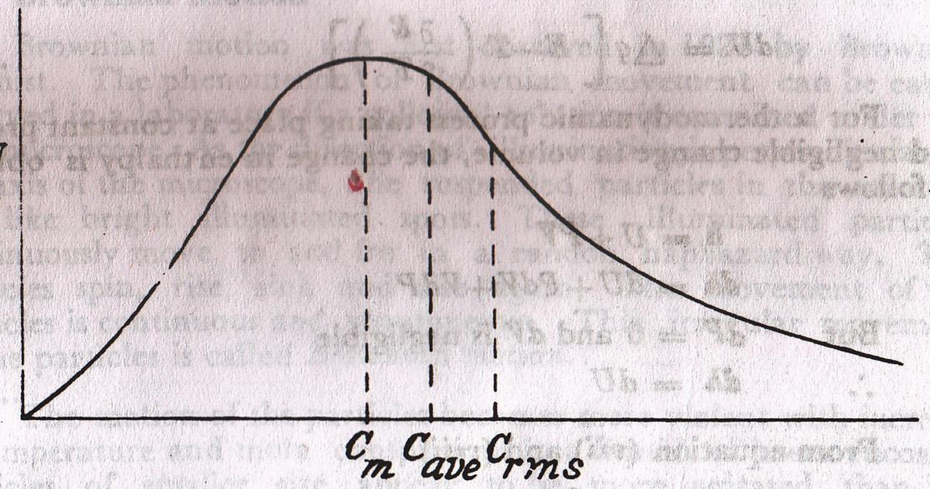


Fig. A-1

A-3 EMF of a Reversible Cell

The first TdS equation is given by

$$T\, dS = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \ldots(i)$$

In the case of a reversible cell composed of solids and liquids in the above equation replace charge q for V and EMF, $-E$ for P.

$$\therefore \quad TdS = C_q\, dT - T\left(\frac{\partial E}{\partial T}\right)_q dq \qquad \ldots(ii)$$

For a reversible cell, in which the *EMF* depends only on temperature,

$$TdS = C_q\, dT - T\left(\frac{\partial E}{\partial T}\right)_q dq \qquad \ldots(iii)$$

For a reversible cell, when a charge $(q_f - q_i)$ is transferred isothermally, taking $TdS = \delta H$, we get

$$\delta H = -T\left(\frac{\partial E}{\partial T}\right)(q_f - q_i) \qquad \ldots(iv)$$

Here $(q_f - q_i)$ is negative when positive charge flows from positive to the negative electrode externally. The work done by the cell,

$$\delta W = -E(q_f - q_i) = -E\triangle q \qquad \ldots(v)$$

Here $\triangle q = (q_f - q_i)$

$$\therefore \quad \delta H = -T\left(\frac{\partial E}{\partial T}\right)\triangle q \qquad \ldots(vi)$$

From the first law of thermodynamics

$$\delta H = dU + \delta W$$

$$\therefore \quad dU = \delta H - \delta W$$

$$dU = \triangle q\left[E - T\left(\frac{\partial E}{\partial T}\right)\right] \qquad \ldots(vii)$$

For a thermodynamic process taking place at constant pressure and negligible change in volume, the change in enthalpy is obtained as follows

$$h = U + PV$$

$$dh = dU + PdV + VdP$$

But $dP = 0$ and dV is negligible

$$\therefore \quad dh = dU \qquad \ldots(viii)$$

From equation (*vii*) and (*viii*)

$$dh = \triangle q\left[E - T\left(\frac{\partial E}{\partial T}\right)\right] \qquad \ldots(ix)$$

dh represents the net transfer of heat between the final and the initial states of the reaction.

From equation (*ix*)

$$\frac{dh}{\triangle q} = E - T\left(\frac{\partial E}{\partial T}\right)$$

or

$$E = \left(\frac{dh}{\triangle q}\right) + T\left(\frac{\partial E}{\partial T}\right)$$

Let $\left(\frac{dh}{\triangle q}\right) = H$

Here H is the heat transferred per unit charge

$$E = H + T\left(\frac{\partial E}{\partial T}\right) \qquad \ldots(x)$$

Equation (*x*) is called Gibbs-Helmholtz equation.

Special cases. (*i*) $\frac{\partial E}{\partial T} = 0$., the temperature of the cell does not change on supplying current.

(*ii*) If $\frac{\partial E}{\partial T}$ is positive, then $E > H$ and the cell has to absorb heat to keep the temperature constant. In this case, the temperature of the cell falls if it supplies current.

(*iii*) If $\frac{\partial E}{\partial T}$ is negative, $E < H$, the cell gives out energy to maintain its temperature or the temperature of the cell increases with the supply of current.

A-4 Brownian Motion

Brownian motion was first observed in 1827 by Brown, a botanist. The phenomenon of Brownian movement can be easily observed in a laboratory if a colloidal solution is examined under an ultramicroscope. As the direction of illumination is perpendicular to the axis of the microscope, the suspended particles in the solution look like bright illuminated spots. These illuminated particles continuously move to and fro in a randon haphazard way. The particles spin, rise, sink and rise again. The movement of the particles is continuous and spontaneous. This irregular movement of the particles is called *Brownian motion.*

The motion of the particles becomes more violent with increase in temperature and more conspicuous in a liquid of lower viscosity. Particles of smaller size appear to be more agitated than the bigger particles. Further, no two particles execute the same type of motion.

The phenomenon of Brownian movement gives a clear picture of the gaseous state of matter. The motion of the molecules of a gas is similar in nature to the Brownian motion of suspended particles in colloidal solution. It may be noted that the laws of Kinetic theory of gases are applicable to Brownian particles also.

A-5 Distribution of Brownian Particles in a Vertical Column

The Brownian particles form a gas in equilibrium under the action of earth's gravitation The concentration of the particles decreases with height due to gravity. Consider two layers of the particles at heights h and $h + dh$. Let P and $P + dP$ be the pressures respectively and ρ the density of the gas at a height h. Consider a unit area of the layer. The force due to gravity acting on the particles between the two layers

$$= (1 \times dh)\,\rho\, g = \ldots dh$$

The net force on the layer

$$=(P+dP)-P+[g\,\rho\,dh]$$

In the equilibrium state, the net force must be equal to zero. Therefore,

$$(P+dP)-P+(g\,\rho\,dh)=0$$

$$dP+g\,\rho\,dh=0$$

or

$$dP=-g\,\rho\,dh \qquad \ldots(i)$$

or

For a perfect gas

$$P=nkT,$$

$$dP=kT\,dn$$

and

$$\rho=mn$$

and

Here n is the number of molecules per unit volume and m is the mass of each molecule.

Substituting these values in equation (*i*)

$$kT\,dn=-g\,mn\,dh$$

$$\frac{dn}{n}=-\left(\frac{mg}{kT}\right)dh$$

Also $k=\frac{R}{N}$, Here N is Avogadro's number

$$\therefore \quad \frac{dn}{n}=-\left(\frac{Nmg}{RT}\right)dh \qquad (ii)$$

Integrating

$$\log n=-\left(\frac{Nmg}{RT}\right)h+K \qquad \ldots(iii)$$

Here, K is a constant

At $h=h_0$, $n=n_0$

$$\therefore \quad \log n_0=-\left(\frac{Nmg}{RT}\right)h_0+K$$

$$\therefore \quad K=\log n_0+\left(\frac{Nmg}{RT}\right)h_0$$

Substituting this value of K in equation (*iii*)

$$\log n=-\left(\frac{Nmg}{RT}\right)h+\left(\frac{Nmg}{RT}\right)h_0+\log n_0$$

$$\log\left(\frac{n}{n_0}\right)=-\left(\frac{Nmg}{RT}\right)(h-h_0) \qquad \ldots(iv)$$

$$\therefore \quad n=n_0\left[e^{-\left(\frac{Nmg}{RT}\right)(h-h_0)}\right] \qquad \ldots(v)$$

A-6. Determination of Avogadro's number (N)

From equation (*iv*)

$$N=\frac{RT\log\left(\frac{n_0}{n}\right)}{mg\,(h-h_0)} \qquad \ldots(vi)$$

The effective mass of the suspended particle,

$$m=\frac{4}{3}\pi a^3(d_1-d_2)$$

Here a is the radius of the particle, d_1 is the density of the particle and d_2 is the density of the intervening fluid

$$\therefore \quad N=\frac{3RT\log\left(\frac{n_0}{n}\right)}{4\pi a^3 g(d_1-d_2)(h-h_0)} \qquad \ldots(vii)$$

From equation (*vii*), the value of N can be calculated if the values of a and d_1 are known.

Determination of d_1. Perrin used the method of finding density (d_1) with a specific gravity bottle. Let m_1 and m_2 be the masses of water and emulsion filling the specific gravity bottle (volume V) and m_3 the mass of the particles left over after dessication in an oven. Taking d as the density of water,

Volume of granules,

$$=\left(\frac{m_1}{d}\right)-\left(\frac{m_2-m_3}{d}\right)$$

$\therefore$ Density of granules,

$$d_1=\frac{m_3}{\left(\frac{m_1}{d}\right)-\left(\frac{m_2-m_3}{d}\right)}$$

or

$$d_1=\frac{m_3\,d}{(m_1+m_3-m_2)} \qquad \ldots(viii)$$

Determination of a. The radius of the particles is determined by Stoke's formula.

The terminal velocity v of the particles is determined by experiment.

$$\therefore \quad 6\pi\eta\,a\,v=\frac{4}{3}\pi a^3(d_1-d_2)g$$

$$\therefore \quad a=\left[\frac{9\eta v}{2(d_1-d_2)g}\right]^{\frac{1}{2}} \qquad \ldots(ix)$$

Substituting these values of d_1 and a in equation (*vii*) the value of Avogadro's number can be calculated. To measure the values of n and n_0 at heights h and h_0, photographs of the suspended particles

are taken and the number of particles in these photographs is counted. The value of Avogadro's number determined by Perrin was found, to be $6{\cdot}82\times10^{26}$ moles/kg-mole which is slightly higher than the present accepted value of $6{\cdot}023\times10^{26}$ molecules/kg-mole.

A-7 Langevin's Theory of Brownian Motion

According to Langevin, the force experienced by a suspended particle is of two kinds :—

(*i*) Frictional force proportional to the velocity,

$$f\left(\frac{dx}{dt}\right) = 6\pi\eta a v$$

(*ii*) Force due to all external influences of the surrounding fluid.

Consider the motion of a particle in a specified direction say x –direction. The force on the particle is given by the equation

$$m\left(\frac{d^2x}{dt^2}\right) = -f\left(\frac{dx}{dt}\right)+F \quad ...(i)$$

Here, $-f\left(\frac{dx}{dt}\right)$ represents the component of the frictiona force in the x— direction. F is the combined force due to other influences. Multiply equation (*i*) by x,

$$mx\left(\frac{d^2x}{dt^2}\right) = -fx\left(\frac{dx}{dt}\right)+Fx \quad ...(ii)$$

Also $$\frac{d}{dt}(x^2) = 2x\left(\frac{dx}{dt}\right) \text{ and } x\left(\frac{dx}{dt}\right) = \frac{1}{2}\frac{d}{dt}(x^2)$$

$$\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right] = 2\left[x\left(\frac{d^2x}{dt^2}\right)+\left(\frac{dx}{dt}\right)^2\right]$$

$$\therefore \quad x\left(\frac{d^2x}{dt^2}\right) = \frac{1}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]-\left(\frac{dx}{dt}\right)^2 \quad ...(iii)$$

Substituting these values in equation (*ii*)

$$\frac{m}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]-m\left(\frac{dx}{dt}\right)^2 = -\frac{f}{2}\frac{d}{dt}(x^2)+Fx \quad ...(iv)$$

Equation (*iv*) represents the motion of a single particle. For all the particles, the mean value can be written as

$$\frac{m}{2}\overline{\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]}-m\overline{\left(\frac{dx}{dt}\right)^2} = -\frac{f}{2}\overline{\frac{d}{dt}(x^2)}+\overline{Fx} \quad ...(v)$$

As the force F varies completely in an irregular manner, it can be assumed that

$$\overline{Fx} = 0$$

Further, from the law of equipartition of velocities,

$$m\overline{\left(\frac{dx}{dt}\right)^2} = kT$$

Also take $\frac{d}{dt}(x^2) = \frac{d}{dt}(\overline{x^2}) = U$

Substituting these values in equation (*v*)

$$\frac{m}{2}\left(\frac{dU}{dt}\right)+\frac{fU}{2} = kT$$

or $$\frac{dU}{dt}+\left(\frac{f}{m}\right)U = \frac{2kT}{m} \quad ...(vi)$$

The general, solution of equation (*vi*) is

$$U = \frac{2kT}{f}+A\left[e^{-\left(\frac{f}{m}\right)t}\right] \quad ...(vii)$$

As the value of m is very small, the value of (f/m) is very large and hence $e^{\left(\frac{-f}{m}\right)t}$ is negligibly small

$$\therefore \quad u = \frac{2kT}{f} = \frac{\overline{d(x^2)}}{dt} \quad ...(viii)$$

For a time interval $t=0$ to $t=\tau$, integrating equation (*viii*) we get

$$\overline{x^2}-\overline{x_0^2} = \left(\frac{2kT}{f}\right)\tau$$

At $t = 0$, $x_0 = 0$ and for small values, x^2 can be written as Δx^2

$$\therefore \quad \overline{\Delta x^2} = \left(\frac{2kT}{f}\right)\tau \quad ...(ix)$$

For each interval of time τ, the displacement Δx of the particle in the x—direction is determined. The mean square value $\overline{\Delta x^2}$ is calculated. In actual practice the particle makes millions of collisions and moves along zig-zag paths. The value $\overline{\Delta x^2}$ is only loosely related to the actual path.

According to Stoke's formula,

$$f\left(\frac{dx}{dt}\right) = 6\pi\eta a v = 6\pi\eta a\left(\frac{dx}{dt}\right)$$

$$\therefore \quad f = 6\pi\eta a$$

$$\therefore \quad \overline{\Delta x^2} = \frac{2kT\tau}{6\pi\eta a} = \frac{kT\tau}{3\pi\eta a} \quad ...(x)$$

or $$\left[\overline{\Delta x^2}\right]^{\frac{1}{2}} = \frac{(kT)^{\frac{1}{2}}(\tau)^{\frac{1}{2}}}{(3\pi\eta a)^{\frac{1}{2}}} \quad ...(xi)$$

This theory indicates that $\overline{\Delta x^2}$ is not dependent on the mass of the particle. In the experiments of Perrin, the masses of the particles varied in the ratio 1 to 15000. However, within the limits of experimental error, the value of Boltzmann's constant k is the same.

Further, $(\overline{\triangle x^2})^{\frac{1}{2}} \propto \tau^{\frac{1}{2}}$

and $\left(\overline{\triangle x^2}\right)^{\frac{1}{2}} \propto \frac{1}{\eta^{\frac{1}{2}}}$

The effect of temperature is not very large because $(\overline{\triangle x^2})^{\frac{1}{2}} \propto T^{\frac{1}{2}}$ However, viscosity decreases rapidly with increase in temperature. Thus, the pure temperature effect is negligibly small in comparison to the effect of viscosity.

Diffusion, fluctuations in concentration and Brownian motion represent a single phenomenon. Diffusion is a macroscopic phenomenon whereas Brownian motion is a microscopic phenomenon.

A-8 Einstein's Theory of Brownian Motion

According to Einstein's theory of transitional Brownian motion, the particles tend to diffuse into the medium in course of time. Consequently, the diffusion coefficient must be related to the Brownian movement.

The diffusion coefficient can be calculated in two different ways :—

(1) From the irregular motion of the suspended particles

(2) From the difference in osmotic pressure caused by the differences in concentration of the suspended particles.

Let D be the diffusion coefficient. Consider an imaginary cylinder with its axis along the x-axis. The end faces P and Q are separated by a distance $\triangle$. Let n_1 and n_2 be molecular concentration at the end faces of the cylinder and A the area of cross-section.

The number of particles crossing the surface P to the right in time $T = \frac{1}{2} n_1 A \triangle$

Similarly, the number of particles crossing the surface Q in the opposite direction $= \frac{1}{2} n_2 A \triangle$

It should be noted that half the particles contained in the imaginary cylinder move towards right whereas the other half move towards left.

The excess number of particles crossing a middle layer to the right $= \frac{1}{2}(n_1 - n_2) A \triangle$

From the definition of diffusion coefficient, the number,

$$\frac{1}{2}(n_1 - n_2) A \triangle = -D \frac{dn}{dx} \tau A$$

Here $\left(\frac{dn}{dx}\right)$ is the concentration gradient.

But $(n_1 - n_2) = -\triangle \frac{dn}{dx}$

$$\therefore \quad -\frac{1}{2} \triangle^2 \left(\frac{dn}{dx}\right) = -D \left(\frac{dn}{dx}\right) \tau$$

$$\therefore \quad \triangle^2 = 2 D \tau$$

or
$$D = \frac{\triangle^2}{2\tau} \qquad \ldots(i)$$

Now, D is to be calculated from the concept of osmotic pressure. If p_1 and p_2 are the osmotic pressures at the end P and Q, then from the gas laws

$$p_1 = n_1 kT$$

$$p_2 = n_2 kT$$

Thus the cylinder experiences a resultant force, $(p_1 - p_2) A = (n_1 - n_2) kTA$ along the +ve x-direction. This force is experienced by the particles contained in the cylinder.

The number of particles in the cylinder

$$= nA \triangle$$

where n is the mean concentration.

Therefore, the force acting on a single particle

$$f' = \frac{(n_1 - n_2) kTA}{nA \triangle} \qquad \ldots(ii)$$

Substituting the value of $(n_1 - n_2) = -\triangle \frac{dn}{dx}$ in equation (ii)

$$f' = -\left(\frac{dn}{dx}\right)\left(\frac{kT}{n}\right)$$

$$\therefore \quad 6\pi\eta a v = -\left(\frac{kT}{n}\right)\left(\frac{dn}{dx}\right)$$

or
$$nv = -\left(\frac{kT}{6\pi\eta a}\right)\left(\frac{dn}{dx}\right) \qquad \ldots(iii)$$

Here nv is the number of particles moving to the right per unit area per second

$$\therefore \quad nv = -D\left(\frac{dn}{d}\right) \qquad \ldots(iv)$$

Equating (iii) and (iv)

$$-D\left(\frac{dn}{dx}\right) = -\left(\frac{kT}{6\pi\eta a}\right)\left(\frac{dn}{dx}\right)$$

or
$$D = \left(\frac{kT}{6\pi\eta a}\right) = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta a}\right) \qquad \ldots(iv)$$

From equations (i) and (iv)

$$\frac{\triangle^2}{2\tau} = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta a}\right)$$

$$\triangle^2 = \frac{RT}{N}\left(\frac{1}{3\pi\eta a}\right) \qquad \ldots(v)$$

Equations (*i*) and (*iv*) have been verified experimentally. Also, with the help of equation (*iv*), the value of Avogadro's number is calculated.

A-9 Brownian Motion of a Galvanometer

In the case of a moving coil galvanometer with a lamp and scale arrangement, the initial position is adjusted so that the spot of light is at the zero mark on the scale. Even when no current passes through the galvanometer coil, it is sometimes noticed that the spot of light has shifted from zero. This is due to the random zig zag collisions of the air molecules with the suspended system. When these collisions produce unequal torques in opposite directions, the suspended system continuously fluctuates and results in unsteady, zero setting. This shift of zero setting is due to Brownian motion of a galvanometer.

For a suspension fibre, the elastic potential energy is $\frac{1}{2} C\theta^2$ where C is the torsional rigidity of the fibre. Similarly, the rotational kinetic energy of the suspended system is $\frac{1}{2} I\omega^2$. The mean elastic potential energy $= \frac{1}{2} C\,\overline{\theta^2}$ and mean rotational kinetic energy $= \frac{1}{2} I\,\overline{\omega^2}$. Each of these quantities are equal to $\frac{1}{2} kT$. Here k is the Boltzmann's constant, T is the temperature in degree kelvin

$$\therefore \qquad \tfrac{1}{2} C\,\overline{\theta^2} = \tfrac{1}{2} kT \qquad \ldots(i)$$

and
$$\tfrac{1}{2} I\,\overline{\omega^2} = \tfrac{1}{2} kT \qquad \ldots(ii)$$

The root mean square angular displacement of the suspended system is given by

$$\theta_{rms} = \sqrt{\overline{\theta^2}} = \sqrt{\frac{\overline{kT}}{C}} \qquad \ldots(iii)$$

For a fine quartz suspension fibre C is approximately equal to 10^{-13} N-m/radian.

and
$$k = 1{\cdot}38 \times 10^{-23}$$

For a room temperature of 300 K.

$$\theta_{rms} = \sqrt{\frac{\overline{kT}}{C}}$$

$$\theta_{rms} = \left[\frac{1{\cdot}38 \times 10^{-23} \times 300}{10^{-13}}\right]^{\frac{1}{2}}$$

$$\theta_{rms} = 2 \times 10^{-4} \text{ radian}$$

If the scale is kept at a distance of one metre from the mirror of the galvanometer, then the displacement of the spot of light from zero is given by

$$2\,(\theta_{rms}) = \frac{dx}{l}$$

$$dx = 4 \times 10^{-4} \text{ m} = 0{\cdot}4 \text{ mm}.$$

For a large value of C, the value of dx increases.

A-10 Johnson Noise

In semiconductors, the two principal sources of noise are (*i*) shot noise and (*ii*) noise due to thermal agitation.

The shot noise or the shot effect is due to the fluctuations caused by the emission of the electrons from the cathode. The thermal noise or the Johnson noise is due to random fluctuations of charge carriers. The thermal noise in semiconductor circuits has been studied experimentally by Johnson.

Consider a transmission line having inductance, capacitance and zero resistance. If after the steady state, the transmission line is isolated, the waves travelling along the line are reflected at the ends and stationary waves are produced. For a velocity v and length l of the transmission line, the frequency of the waves,

$$f_0 = \frac{v}{2l}$$

The harmonic frequencies will be $2f_0$, $3f_0$ etc. Each of the waves has an energy kT associated with it (half the energy is magnetic and half is electrostatic).

It has been observed that the noise in the bandwidth 1000 Hz to 2000 Hz is equal to that in the bandwidth 15000 Hz to 16000 Hz. It means that the noise spectrum is uniform. In practice, shot noise and Johnson noise can be reduced by suitably treating the semiconductor surfaces.

APPENDIX II

Miscellaneous Numerical Problems

Example A-1 *Calculate the total random kinetic energy of one* gram-mole *of oxygen at 330* K.

[$R = 8{\cdot}31$ J/mole-K]

[*I.A.S. 1983*]

Total random kinetic of one gram mole of oxygen,

$$U = \frac{3}{2} RT$$

$$U = \frac{3}{2} \times 8{\cdot}31 \times 300$$

$$U = 3{\cdot}739 \times 10^3 \text{ J}$$

Example A-2 *The Van der Waals' constants a and b for 1* gram *molecule of hydrogen are* $a = 0{\cdot}245$ atoms-litre^2-mole^{-2}

$b = 2{\cdot}67 \times 10^{-2}$ litre-mole^{-1}

Calculate the critical temperature. (*Rajasthan 1981*)

Critical temperature

$$T_c = \frac{8a}{27\,Rb}$$

Here $a = 0{\cdot}245 \times 76 \times 13{\cdot}6 \times 980 \times 10^6$ dynes-cm^4-mole^{-2}

$b = 2{\cdot}67 \times 10^{-2}$ litre-mole^{-1}

$= 2{\cdot}67 \times 10^{-2} \times 10^3$ cm^3 mole^{-1}

$R = 8{\cdot}31 \times 10^7$ ergs/mole-K

$$\therefore \quad T_c = \frac{8 \times 0{\cdot}245 \times 76 \times 13{\cdot}6 \times 980 \times 10^6}{27 \times 8{\cdot}31 \times 10^7 \times 2{\cdot}67 \times 10^{-2} \times 10^3}$$

$$T_c = 33{\cdot}14 \text{ K} = -239{\cdot}86°\text{C}$$

Example A-3 *The mean kinetic energy of molecules of hydrogen at 0°C is* $5{\cdot}64 \times 10^{-21}$ J *and molar gas constant is 8·32* J/mole—K. *Calculate Avogadro's number.*

[*Delhi, 1981*]

$$E = \frac{3}{2} kT$$

$$E = \frac{3}{2}\left(\frac{R}{N}\right) T$$

or
$$N = \frac{3RT}{2E}$$

Here $E = 5{\cdot}64 \times 10^{-21}$ J

$R = 8{\cdot}32$ J/mole—K

$T = 273$ K

$$\therefore \quad N = \frac{3 \times 8{\cdot}32 \times 273}{2 \times 5{\cdot}64 \times 10^{-21}}$$

$$N = 6{\cdot}182 \times 10^{23}$$

Example A-4 *The diameter of the molecule of a gas is* 2×10^{-8} cm *and Boltzmann's constant is* $1{\cdot}38 \times 10^{-23}$ J/K. *Calculate the mean free path at NTP.*

[*Delhi (Hons.) 1984*]

Here $d = 2 \times 10^{-8}$ cm $= 2 \times 10^{-10}$ m

$k = 1{\cdot}38 \times 10^{-23}$ J/K

Let n be the number of the molcules per cubic meter.

$$PV = RT$$

$$PV = NkT$$

$$n = \left(\frac{N}{V}\right) = \frac{P}{kT}$$

At NTP

$$n = \frac{0{\cdot}76 \times 13{\cdot}6 \times 10^3 \times 9{\cdot}8}{1{\cdot}38 \times 10^{-23} \times 273}$$

$$n = 2{\cdot}688 \times 10^{25}$$

Mean free path

$$\lambda = \frac{1}{\pi d^2 n} = \frac{1}{3{\cdot}14 \times (2 \times 10^{-10})^2 \times 2{\cdot}688 \times 10^{25}}$$

$$\lambda = 2{\cdot}961 \times 10^{-7} \text{ m}$$

Example A-5 *Prove that*

$$\frac{K}{\eta C_v} = 1 \text{ for a gas}$$

(*Rajasthan 1981*)

The expression for coefficient of viscosity

$$\eta = \frac{m C}{3 \lambda} \qquad \ldots(i)$$

The coefficient of thermal conductivity

$$K = \frac{mC C_v}{3 \lambda} \qquad \ldots(ii)$$

Dividing (*ii*) by (*i*)

$$\frac{K}{\eta} = C_v$$

or $$\frac{K}{\gamma_i C_r} = 1$$

Example. A 6. *For oxygen at standard conditions, calculate (a) Collision frequency of the molecules and (b) the mean free path. Given at standard conditions for oxpgen,*

(i) the number of molecules per cubic metre $= 3\times10^{25}$

(ii) Diameter of oxygen molecule $= 3{\cdot}6\times10^{-10}$ m

(Delhi (Hons.) 1984)

Here $k = 1{\cdot}38\times10^{-23}$

and $m = \dfrac{32}{6{\cdot}023\times10^{26}} = 5{\cdot}31\times10^{26}$ kg

Average speed of oxygen molecule at 0°C (273 K)

$$v = \sqrt{\frac{8\,k\,T}{\pi\,m}}$$

$$v = \sqrt{\frac{8\times1{\cdot}38\times10^{-23}\times273}{3{\cdot}14\times5{\cdot}31\times10^{-26}}}$$

$$v = \mathbf{426}\ \text{m/s}$$

Also $d = 3{\cdot}6\times10^{-10}$ m

$n = 3\times10^{25}$ molecules/m^3

(*a*) Colllsion frequency (number of collisions per second)

$$= \pi d^2\, vn$$

$$= 3{\cdot}14\,(3{\cdot}6\times10^{-10})^2\times426\times3\times10^{25}$$

$$= \mathbf{5{\cdot}2\times10^{9}}$$

(*b*) Mean free path

$$\lambda = \frac{1}{\pi d^2\, n} = \frac{1}{3{\cdot}14\times(3{\cdot}6\times10^{-10})^2\times3\times10^{25}}$$

$$\lambda = \mathbf{8{\cdot}19\times10^{-8}}\ \text{m}.$$

Example A-7 *Calculate the Fermi energy and pressure at absolute zero for copper assuming that it has one free electron per atom. Density of copper* $= 9000$ kg/m^3 *and atomic weight* $= 63{\cdot}5$.

[Delhi (Hons) 1983]

Taking one free electron per atom, 63·5 kg of copper contains $6{\cdot}023\times10^{26}$ free electrons.

Density of copper $= 9000$ kg/m^3

$\therefore$ $$V = \frac{63{\cdot}5}{9000}$$

$$\frac{N}{V} = \frac{6{\cdot}023\times10^{26}\times9000}{63{\cdot}5}$$

or $$\frac{N}{V} = 85{\cdot}36\times10^{27}$$

$$E_F = \frac{h^2}{8m}\left[\left(\frac{3}{\pi}\right)\left(\frac{N}{V}\right)\right]^{2/3}$$

$$E_F = \left[\frac{(6{\cdot}624\times10^{-34})^2}{8\times9\times10^{-31}}\right]\left[\frac{3\times85{\cdot}36\times10^{27}}{3{\cdot}14}\right]^{2/3}$$

$$E_F = 11{\cdot}46\times10^{-19}\ \text{J}$$

$$E_F = \frac{11{\cdot}46\times10^{-19}}{1{\cdot}6\times10^{-19}}\ \text{eV}$$

$$E_F = \mathbf{7{\cdot}163}\ \text{eV}$$

Pressure, $$p = \frac{2U}{3V}$$

$$p = \frac{2N\,E_F}{3V}$$

$$p = \left(\frac{2}{3}\right)\left(\frac{N}{V}\right)E_F$$

$$p = \left(\frac{2}{3}\right)85{\cdot}36\times10^{27}\times11{\cdot}46\times10^{-19}$$

$$p = \mathbf{6{\cdot}5215\times10^{10}}\ \text{N/m}^2$$

Example A-8 *A gas occupying 1 litre at 80 cm of Hg pressure is expanded adiabatically to 1190 c.c. If the pressure falls to 60 cm of Hg in the process, deduce the value of* γ.

[Delhi, 1981]

Here $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$$\left(\frac{P_1}{P_2}\right) = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

Taking logs,

$$\log\left(\frac{P_1}{P_2}\right) = \gamma\left(\log\frac{V_2}{V_1}\right)$$

or $$\gamma = \frac{\log\left(\dfrac{P_1}{P_2}\right)}{\log\left(\dfrac{V_2}{V_1}\right)}$$

$$\gamma = \frac{\log\left(\dfrac{80}{60}\right)}{\log\left(\dfrac{1190}{1000}\right)}$$

$$\gamma = \frac{0{\cdot}1249}{0{\cdot}0755}$$

$$\gamma = \mathbf{1{\cdot}787}$$

Example A-9. *Calculate the work done when a gram molecule of an ideal gas expands isothermally at 27°C to double its original volume.* [$R = 8{\cdot}3$ J/deg mole]

[Delhi, 1983]

Workdone $= \int_{V_1}^{V_2} P\,dV$

But $PV = RT$

$$P = \frac{RT}{V}$$

$$W = RT \int_{V_1}^{V_2} \left(\frac{dV}{V}\right)$$

or $$W = RT \log_e \left(\frac{V_2}{V_1}\right)$$

Here $\frac{V_2}{V_1} = 2$

$R = 8{\cdot}3$ J/deg mole

$T = 273+27 = 303$ K

$W = 8{\cdot}3 \times 300 \log_e 2$

$W = \mathbf{1725{\cdot}9\ J}$

Example A-10. *The initial temperature of a gas is 27°C. Calculate the rise in temperature when the gas is compressed suddenly to 8 times its original pressure ($\gamma = 1{\cdot}5$)* *(Delhi, 1984)*

For an adiabatic process,

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

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^2$$

Here $\frac{P_2}{P_1} = 8$ and $T_1 = 273+27 = 300$ K

$\gamma = 1{\cdot}5$

$\therefore$ $$(8)^{\gamma-1} = \left(\frac{T_2}{300}\right)^{\gamma}$$

$$(8)^{0.5} = \left(\frac{T_2}{300}\right)^{1.5}$$

$$0{\cdot}5 \log 8 = 1{\cdot}5\ [\log T_2 - \log 300]$$

$$0{\cdot}5\ (0{\cdot}9031) = 1{\cdot}5 \log T_2 - 1{\cdot}5 \times 2{\cdot}4771$$

$$1{\cdot}5 \log T_2 = 0{\cdot}5 \times 0{\cdot}9031 + 1{\cdot}5 \times 2{\cdot}4771$$

$$1{\cdot}5 \log T_2 = 0{\cdot}4516 + 3{\cdot}7157$$

$$1{\cdot}5 \log T_2 = 4{\cdot}1673$$

$$\log T_2 = \frac{4{\cdot}1673}{1{\cdot}5}$$

$$\log T_2 = 2.7782$$

$$T_2 = \mathbf{600\ K}$$

$$T_2 = \mathbf{327°C.}$$

Example A-11 *A Carnot engine has an efficiency of 30% when the temperature of the sink is 27°C. What must be the change in temperature of the source to make its efficiency 50%.* *[Rajasthan, 1981]*

In the first case,

$$\eta = 30\% = 0{\cdot}3, \quad T_2 = 300\ \text{K}, \quad T_1 = ?$$

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

$$0{\cdot}3 = 1 - \frac{300}{T_1}$$

$$T_1 = \mathbf{428{\cdot}57\ K}$$

In the second case,

$$\eta' = 50\% = 0{\cdot}5, \quad T_2 = 300\ \text{K}, \quad T_1' = ?$$

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

$$0{\cdot}5 = 1 - \frac{300}{T_1'}$$

$$T_1' = 600\ \text{K}$$

Increase in temperature

$$= \mathbf{171{\cdot}43\ K}$$

Example A-12 *One of the most efficient engines ever developed by a manufacturer has an efficiency of 40% while operating between 2100 K and 700 K. What percentage is this efficiency of the maximum possible efficiency of an engine working between these very temperatures ?* *[Delhi, 1983]*

$$T_1 = 2100\ \text{K}$$

$$T_2 = 700\ \text{K}$$

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

or $$\eta = 1 - \left(\frac{700}{2100}\right) = \frac{2}{3}$$

Actual efficiency, $\eta' = 40\% = \frac{2}{5}$

$$\frac{\eta'}{\eta} = \frac{2/5}{2/3} = \frac{3}{5} = \mathbf{60\%}$$

Example A-13 *An inventor claims to have developed an engine working between 600 K and 300 K capable of having an efficiency of 52%. Comment on his claim.* *[IAS, 1983]*

$$T_1 = 600\ \text{K}, \quad T_2 = 300\ \text{K}$$

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

$$\eta = 1-\left(\frac{300}{600}\right) = \frac{1}{2}$$

i.e. $\eta = 50\%$.

The efficiency claimed = 52%

It means that the efficiency of the engine is more than the efficiency of a carnot's engine working between the same two temperature limits. But no engine can have an efficiency more than a carnot's engine, so his **claim is invalid**.

Example A-14. *A carnot's engine absorbs 10^4 calories of heat from a reservoir at 627°C and rejects heat to a sink at 27°C. What is its efficiency ? How much work does it perform ?* [$J = 4{\cdot}2$ J/Caloric] *[Delhi. 1984]*

Here $T_1 = 627+273 = 900$ K

$T_2 = 27+273 = 300$ K

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

$$\eta = 1-\frac{300}{900}$$

$$\eta = \frac{2}{3} \text{ or } 66{\cdot}67\%$$

Also $\frac{H_1}{H_2} = \frac{T_1}{T_2}$

Here $H_1 = 10^4$ Calories

$\therefore$ $H_2 = \frac{H_1 \times T_2}{T_1}$

$$H_2 = \frac{10^4 \times 300}{900} = \frac{10^4}{3} \text{ Calories}$$

Work done $W = H_1 - H_2$

$$W = 10^4 - \left(\frac{10^4}{3}\right)$$

$$W = \frac{2\times10^4}{3} \text{ Calories}$$

$$W = \frac{2\times10^4}{3}\times 4{\cdot}2$$

$$W = 2{\cdot}8\times10^4 \text{ J}.$$

Example A-15 *A 100 k-W engine is operating between 217°C and 17°C. Calculate*

(i) the amount of heat absorbed

(ii) the amount of heat rejected and

(iii) the efficiency of the engine. *(Rajasthan, 1981)*

$W = 100$ kW $= 10^5$ watts $= 10^5$ J/s

$T_1 = 217°C = 400$ K

$T_2 = 17°C = 300$ K

Efficiency,

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

$$\eta = 1-\frac{300}{400}$$

$$\eta = 0{\cdot}25 = 25\%$$

Also $\frac{H_1}{H_2} = \frac{T_1}{T_2} = \frac{400}{300} = \frac{4}{3}$

or $\left(\frac{H_1}{H_2}\right)-1 = \left(\frac{4}{3}\right)-1$

$$\frac{H_1-H_2}{H_2} = \frac{1}{3}$$

But $W = H_1-H_2 = 10^5$ J/s

$\therefore$ $\frac{10^5}{H_2} = \frac{1}{3}$

$$H_2 = 3\times10^5 \text{ J/s}$$

But $\frac{H_1}{H_2} = \frac{4}{3}$

$$H_1 = \left(\frac{4}{3}\right)H_2 = \left(\frac{4}{3}\right)\times3\times10^5$$

or $H_1 = 4\times10^5$ J/s

Hence (*i*) Amount of heat absorbed per second

$= 4\times10^5$ J/s

(*ii*) Amount of heat rejected per second

$= 3\times10^5$ J/s

(*iii*) Efficiency of the engine

$= 0{\cdot}25 = 25\%$

Example A-16 *Calculate the change in entropy when 10 g of water at 60°C is mixed with 30 g of water at 20°C* *[Delhi (Hons) 1982]*

(*i*) $m_1 = 10$ g, $T_1 = 333$ K°

$m_2 = 30$ g, $T_2 = 293$ K°

Let the final temperatine be T K°

$$m_1 s\,(T_1-T) = m_2 s\,(T-T_2)$$

$$10\times1\times(333-T) = 30\times1\,(T-293)$$

$$T = 303 \text{ K°}$$

(*ii*) Change in entropy when the temphature of 10 g of water changs from 333 K to 303 K

$$= \frac{\delta H}{T} = ms\int_{T_1}^{T}\frac{dT}{T}$$

$$= 10\times 1\times \log_e \frac{303}{333}$$

$$= 10\times 2{\cdot}3026\times \log_{10}\left(\frac{303}{333}\right)$$

$$= -0{\cdot}9443 \text{ cal/K°}$$

Nagative sign indicates decrease in entropy.

(*iii*) Change in entropy when the temperature of 30 g of water change from 293 K° to 303 K°,

$$= \frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 30\times 1.\log_e \frac{303}{293}$$

$$= 30\times 2{\cdot}3026 \log_{10}\frac{303}{293}$$

$$= +1{\cdot}002 \text{ cal/K°}$$

The total gain in entropy of the system

$$= +1{\cdot}0020-0{\cdot}9443$$

$$= \mathbf{0{\cdot}0577 \text{ cal/K°}}$$

Example A-17 *Calculate the increase in entropy of 10* kg *of water at 100°C when it changes to vapour.* [*Delhi (Hons) 1983*]

Increase in entropy when 10 kg of water at 100°C is changed into vapour

$$dS = \frac{\delta H}{T} = \frac{10\times 10^3\times 1\times 540}{373}$$

$$dS = \mathbf{14{,}477 \text{ cal/K}}$$

Example A-18 *When 50 g of water is heated from 10°C to 90°C, by how much does its entropy change?* [*Delhi, 1983*]

Here $T_1 = 273+90 = 363$ K

$T_2 = 273+10 = 283$ K

Increase in entropy when 50 g of water is heated from 10°C to 90°C

$$dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$$

$$dS = ms\times 2{\cdot}3026 \log\left(\frac{T_2}{T_1}\right)$$

$$dS = 50\times 1\times 2{\cdot}3026 \log\left(\frac{363}{283}\right)$$

$$dS = \mathbf{12{\cdot}448 \text{ cal/K}}$$

Example A-19 *Calculate the change in entropy when 10 grams of ice at 0°C is converted into steam at 100°C.* [*Delhi, 1981*]

(1) Increase in entropy when 10 grams of ice at 0°C is converted into water at 0°C.

$$dS = \frac{\delta H}{T}$$

$$= \frac{10\times 80}{273} = 2{\cdot}93 \text{ cal/K}$$

(2) Increase in entropy when the temperature of 10 g of water is raised from 0°C to 100°C

$$dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$$

$$= ms\times 2{\cdot}3026 \log_{10}\left(\frac{T_2}{T_1}\right)$$

$$= 10\times 1\times 2{\cdot}3026 \log_{10}\left(\frac{373}{273}\right)$$

$$= 3{\cdot}12 \text{ cal/K}$$

(3) Increase in entropy when 10 g of water at 100°C is converted into steam at 100°C

$$dS = \frac{\delta H}{T}$$

$$= \frac{10\times 540}{373} = 14{\cdot}47 \text{ cal/K}$$

Total increase in entropy $= 2{\cdot}93+3{\cdot}12+14{\cdot}47$

$$= \mathbf{20{\cdot}52 \text{ cal/K}}.$$

Example A-20 *Calculate the change in entropy of 1 gram of nitrogen when its temperature rises from 50°C to 100°C while its volume is kept constant. Molar specific heat, $C_v = 0{\cdot}18$ and molecular weight of nitrogen is 28.* [*Delhi, 1981*]

Specific heat of nitrogen $= \frac{C_v}{28} = \left(\frac{0{\cdot}18}{28}\right)$

Change in entropy, $dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$

$$dS = \frac{1\times 0{\cdot}18}{28}\int_{T_1}^{T_2}\frac{dT}{T}$$

$$dS = \left(\frac{0{\cdot}18}{28}\right)\int_{323}^{373}\frac{dT}{T}$$

$$dS = \left(\frac{0.18}{28}\right) \times 2.3026 \log_{10}\left(\frac{373}{323}\right)$$

$$dS = \frac{0.18 \times 2.3026 \times 0.0625}{28}$$

$$dS = 9.253 \times 10^{-4} \text{ cal/K}.$$

Example A-21 *Calculate the temperature at which ice will freeze if the pressure is increased by 135·2* atmospheres. *Given that the increase in the specific volume when 1* gram *of water freezes into ice is 0·091* cm^3. *Latent heat of fusion of ice is 80* cal/gram.

[*Delhi, 1981*]

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

Here
$dP = 135.2$ atmospheres
$dP = 135.2 \times 1.013 \times 10^6$ dynes/cm^2
$V_2 - V_1 = -0.091$ cm^3
$L = 80$ cal/g
$L = 80 \times 4.18 \times 10^7$ ergs/g
$T = 273$ K

$$\therefore \quad d = T\frac{(dP)\,T\,(V_2 - V_1)}{L}$$

$$dT = \frac{135.2 \times 1.013 \times 10^6 \times 273 \times (-0.091)}{80 \times 4.18 \times 10^7}$$

$$dT = -1 \text{ K}$$

or
$$dT = -1°C$$

Therefore the temperature at which ice will freeze is

$-1°C$ or 272 K.

Example A-22 *1 kg of water at 273* K *is brought in contact with a heat reservoir at 373* K. *What is the change in entropy of water as its temperature reaches 373* K ?

[*IAS, 1983*]

Increase in entropy when the temperature of 1 kg of water is raised from 273 K to 373 K

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$m = 1$ kg, $s = 10^3$ cal/kg-K,

$$dS = ms \times 2.3026 \log_{10}\left(\frac{T_2}{T_1}\right)$$

$$dS = 1 \times 10^3 \times 2.3026 \log_{10}\left(\frac{373}{273}\right)$$

$$dS = 312 \text{ cal/K}.$$

Example A-23. *Calculate the change in entropy, when 0·0273* kg *of ice of 0°C is converted into water at the same temperature,*

[*Delhi, 1984*]

Here
$m = 0.0273$ kg
$L = 80$ Cal/g $= 80 \times 10^3$ Cal/kg
$T = 273$ K

$$dS = \frac{\delta H}{T} \qquad d'_s = \frac{mL}{T}$$

$$dS = \frac{0.0273 \times 80 \times 10^3}{273}$$

$dS = 8$ Cal/K $\quad dS = 8 \times 4.2 = 33.6$ J/K.

Example A-24 *If the initial temperature is 27°C, Calculate the drop in temperature produced by adiabatic throttling in the case of oxygen when the pressure is reduced by 50 atmospheres. Given*

$a = 13.2 \times 10^{-2}$ Nm^4 $(mole)^{-2}$
$b = 31.2 \times 10^{-6}$ m^3 $(mole)^{-1}$
$R = 8.3$ JK^{-1} $(mole)^{-1}$
$C_p = 3.5\,R$ [*Delhi (Hons) 1982*]

$$T = \left(\frac{\delta P}{JMC_p}\right)\left(\frac{2a}{RT} - b\right)$$

Here $\delta P = 50$ atmorpheres
$= 50 \times 0.76 \times 13.6 \times 10^3 \times 9.8$ N/m^2
$J = 4.2$ J/cal
$M = 32$
$C_p = 3.5R = 3.5 \times 8.3$ JK^{-1} $(mole)^{-1}$
$T = 300$ K°

$$\delta T = \left(\frac{50 \times 0.76 \times 13.6 \times 10^3 \times 9.8}{4.2 \times 32 \times 3.5 \times 8.3}\right)\left(\frac{2 \times 13.2 \times 10^{-2}}{8.3 \times 300} - 31.2 \times 10^{-6}\right)$$

$\delta T = 0.0969$ K°

Example A-25 *For a metallic copper disc at 300* K, *the following values are known*

$C_P = 24.5$ J/mol K
$\alpha = 50.4 \times 10^{-6}$ K^{-1}

Isothermal compressibility, $K = 7.78 \times 10^{-12}$ N/m^2
$V = 7.06$ cm^3/mol

Determine C_V.

$$C_P - C_V = TE\,\alpha^2\,V$$

and
$$E = \frac{1}{K}$$

$$\therefore \quad C_P - C_V = \frac{T\,V\,\alpha^2}{K}$$

$V = 7.06$ cm^3/mol $= 7.06 \times 10^{-6}$ m^3/mol

$$C_P - C_V = \frac{300 \times 7.06 \times 10^{-6} \times (50.4 \times 10^{-6})^2}{7.78 \times 10^{-12}}$$

$C_P - C_V = 0.6915$ J/mol-K

$$C_V = C_P - 0{\cdot}6915$$
$$C_V = 24{\cdot}5 - 0{\cdot}6915$$
$$C_V = 23{\cdot}8085 \text{ J/mol-K}$$

Example A-26 *Calculate the drop in temperature produced by adiabatic throttling process in the case of oxygen when the pressure is reduced by 50 atmospheres. Initial temperature of the gas is 27°C. Given that the gas obeys Van der Waal's equation and*

$$a = 1{\cdot}32 \times 10^{12} \text{ cm}^4 \text{ dynes/mole}^2$$
$$b = 31{\cdot}2 \text{ cm}^3\text{/mole}$$

and $C_p = 7$ cal/mole-K

(Rajasthan, 1981)

Here
$$\frac{\delta T}{\delta P} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$
$$\delta_T = \frac{\delta P}{C_p}\left[\frac{2a}{RT} - b\right]$$
$$\delta P = 50 \text{ atmospheres}$$
$$= 50 \times 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$C_p = 7 \text{ cal/mole-K}$$
$$= 7 \times 4{\cdot}2 \times 10^7 \text{ ergs/mole-K}$$
$$T = 27°\text{C} = 300 \text{ K}$$
$$R = 8{\cdot}31 \times 10^7 \text{ ergs/mole-K}$$

$$\therefore \quad \delta T = \left(\frac{50 \times 76 \times 13{\cdot}6 \times 980}{7 \times 4{\cdot}2 \times 10^7}\right)\left(\frac{2 \times 1{\cdot}32 \times 10^{12}}{8{\cdot}31 \times 10^7 \times 300} - 31{\cdot}2\right)$$
$$\delta T = \left(\frac{0{\cdot}5064}{7 \times 4{\cdot}2}\right)\left(317{\cdot}7 - 31{\cdot}2\right)$$
$$\delta T = 4{\cdot}935 \text{ K}$$
$$= 4{\cdot}935 \text{ °C}$$

Example A-27 *Considering mercury at 0°C and 1 atmospheric pressure, determine* $\gamma(C_P/C_V)$. *Given* $C_P = 28{\cdot}0$ J/mol K, *specific volume* $V = 1{\cdot}47 \times 10^{-5}$ m³/mol, *volume expansivity* $\beta = 1{\cdot}81 \times 10^{-6}$ K^{-1} *and compressibility is* $3{\cdot}94 \times 10^{-6}$ atm^{-1} ($3{\cdot}89 \times 10^{-11}$ *Pa*$^{-1}$).

[Delhi (Hons.) 1984]

$$C_P - C_V = \frac{TV\beta^2}{k}$$

Here
$$T = 273 \text{ K}, \quad V = 1{\cdot}47 \times 10^{-5} \text{ m}^3\text{/mol}$$
$$\beta = 1{\cdot}81 \times 10^{-6} \text{ K}^{-1}$$
$$k = 3{\cdot}89 \times 10^{-11} \text{ Pa}^{-1}$$

$$\therefore \quad \frac{TV\beta^2}{k} = \frac{273 \times 1{\cdot}47 \times 10^{-5} \times (1{\cdot}81 \times 10^{-6})}{3{\cdot}89 \times 10^{-11}}$$
$$= 338 \times 10^{-6}$$
$$C_V = C_P - 338 \times 10^{-6} = 28 - 338 \times 10^{-6}$$

$$= 27{\cdot}999662 \text{ J mol K}$$
$$\gamma = \frac{C_P}{C_V} = \frac{28}{27{\cdot}999662} = 1$$

Example A-28 *Calculate the radius of an oxygen molecule if its coefficient of thermal conductivity*

$$K = 24 \times 10^{-3} \text{ J/m-s-K at } 0°\text{C}$$

and $C_v = 20{\cdot}9 \times 10^3$ J/kilo-mole-K,

Boltzmann's constant $k = 1{\cdot}38 \times 10^{-23}$ J/K *and mass of an oxygen molecule*

$$m = 5{\cdot}31 \times 10^{-26} \text{ kg}$$

(Rajasthan, 1981)

$$K = \frac{mC\,C_v}{3(\sqrt{2})\pi\sigma^2}$$

But $\frac{1}{2}mC^2 = \frac{3}{2}kT$ or $C = \sqrt{\frac{3kT}{m}}$

$$\sigma^2 = \frac{mC\,C_v}{3 \times 1{\cdot}414 \times 3{\cdot}142 \times K}$$
$$\sigma^2 = \frac{(\sqrt{3kTm})\,C_v}{3 \times 1{\cdot}414 \times 3{\cdot}142 \times K}$$
$$\sigma^2 = \frac{[3 \times 1{\cdot}38 \times 10^{-23} \times 273 \times 5{\cdot}31 \times 10^{-26}]^{1/2} \times 20{\cdot}9 \times 10^3}{3 \times 1{\cdot}414 \times 3{\cdot}142 \times 24 \times 10^{-3}}$$

or $\sigma = 3{\cdot}036 \times 10^{-11}$ m

Example A-29 *If Wien's constant* $b = 0{\cdot}3$ cm-K°, *calculate the temperature of the sun whose raditaion has maximum energy at wavelength* $\lambda = 5500$ Å. *(Rajasthan, 1981)*

According to Wien's displacement law
$$\lambda_m T = \text{constant} = b$$
$$T = \frac{b}{\lambda_m}$$

Here
$$b = 0{\cdot}3 \text{ cm-K}$$
$$\lambda_m = 5500 \text{ Å} = 5500 \times 10^{-8} \text{ cm}$$

$$\therefore \quad T = \frac{0{\cdot}3}{5500 \times 10^{-8}}$$
$$T = 5455 \text{ K}$$

Example. A-30 *Deduce the temperature at which a black body loses thermal energy at the rate of I* watt/cm².

(Rajasthan, 1981)

$$R = 1 \text{ watt/cm}^2 = 10^4 \text{ watts/m}^2$$
$$R = \sigma T^4$$
$$T^4 = \left(\frac{R}{\sigma}\right)$$

$$T = \left(\frac{R}{\sigma}\right)^{1/4}$$

$$T = \left[\frac{10^4}{5{\cdot}672 \times 10^{-8}}\right]^{1/4}$$

$$T = 648 \text{ K.}$$

Example A-31 *If a black body at a temperature 6174 K emits 4700 Å with maximum energy; calculate the temperature at which it will emit a wave length of $1{\cdot}4 \times 10^{-5}$ m with maximum energy.*

[Delhi (Hons) 1983]

According to Wien's displacement law

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

$$\lambda_m T = \lambda_m' T'$$

$$T' = \frac{\lambda_m T}{\lambda_m'} = \frac{4700 \times 10^{-10} \times 6174}{1{\cdot}4 \times 10^{-5}}$$

$$T' = 207{\cdot}27 \text{ K}$$

Example A-32 *Assume the Sun to be a black-body at temperature 5800 K. Use Stefan's law to show that the total radiant energy emitted by Sun per second is $3{\cdot}95 \times 10^{26}$ J. Also show that the rate at which energy is reaching the top of earth's atmosphere is 1·4 k W-m^{-2}.*

[Delhi (Hons) 1984]

Here radius of the sun, $r = 7 \times 10^8$ m

Surface area of the sun, $A = 4\pi r^2$

$$= 4 \times 3{\cdot}142 \times (7 \times 10^8)^2 \text{ m}^2$$

$\sigma = 5{\cdot}672 \times 10^{-8}$ *SI* units

$T = 5800$ K

Total energy emitted by Sun per second

$$U = A \sigma T^4$$

$$U = 4 \times 3{\cdot}142 \times (7 \times 10^8)^2 \times 5{\cdot}672 \times 10^{-8} \times (5800)^4$$

$$U = 3{\cdot}95 \times 10^{26} \text{ J}$$

Distance of the earth's atmosphere from the Sun

$$= r_1 = 1{\cdot}5 \times 10^{11} \text{ m}$$

Energy reaching per unit area per second,

$$P = \frac{U}{4\pi r_1^2}$$

$$R = \frac{3{\cdot}95 \times 10^{26}}{4 \times 3{\cdot}142 \times (1{\cdot}5 \times 10^{11})^2}$$

$$R = 1{\cdot}3968 \times 10^3 \quad \text{W/m}^2$$

$$R = 1{\cdot}3968 \text{ kW/m}^2$$

or $R \approx 1{\cdot}4 \text{ kW/m}^2$.

Example A-33. *Calculate the energy of 5 gram molecules of ozone (O_3) at 27°C. Given $R = 8{\cdot}3$ J/g-mole/°K.*

[Lucknow, 1990]

Here $U = n\left[\frac{3}{2} RT\right]$

$n = 5$

$R = 8{\cdot}3 \text{ J/g} - \text{mole/°K}$

$T = 27 + 273 = 300$ K

$$U = 5 \times \left(\frac{3}{2}\right) \times 8{\cdot}3 \times 300$$

$$U = 1{\cdot}8675 \times 10^4 \text{ J}$$

Example A-34. *Calculate the pressure required to lower the melting point of ice by 1°C. Given*

$L = 79{\cdot}6$ cal/g. Specific volumes of water at 0°C = 1 cm^3.

Specific volume of ice, at 0°C = 1·091 cm^3. 1 atwospheric pressure = $1{\cdot}013 \times 10^6$ dyne/cm^2.

[Delhi 1990]

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$dT = -1$ K

$T = 273$ K

$V_2 - V_1 = -0{\cdot}091$ cm^3

$L = 79{\cdot}6$ cal/g

$= 79{\cdot}6 \times 4{\cdot}18 \times 10^7$ ergs/g

$$dP = \frac{L\,dT}{T[V_2 - V_1]} = \frac{79{\cdot}6 \times 4{\cdot}18 \times 10^7 \times 1}{273 \times 0{\cdot}091} \text{ dynes/cm}^2$$

$$dP = 1{\cdot}33932 \times 10^8 \text{ dynes/cm}^2$$

$$dP = \frac{1{\cdot}33932 \times 10^8}{1{\cdot}013 \times 10^6} \text{ atmospheres}$$

$dP = 132{\cdot}21$ atmospheres

$\therefore$ Pressure repuired $= 132{\cdot}21 + 1 = 133{\cdot}21$ **atmospheres**

Example A-35. *A black body with temperature 127°C is put in an evacuated enclosure whose walls are blackened and maintained at 27°C. What is net amount of energy lost by body per second per unit area.*

Stefan's constants $\sigma = 5{\cdot}672 \times 10^{-8}$ SI units

[Lucknow 1990]

Here, $T_1 = 273 + 127 = 400$ K

$$T_2 = 273+27 = 300\ \text{K}$$

$$\sigma = 5{\cdot}672\times10^{-8}\ \text{SI units}$$

$$R = \sigma[T_1^4 - T_2^4]$$

$$R = 5672\times10^{-8}\ [(400)^4 - (300)^4]$$

$$R = \mathbf{992{\cdot}6\ watts/m^2}$$

Example A 36. *A Carnot's engine whose low temperature reservoir is 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the source reservoir be inereased ?* [*Delhi 1990*]

Here $T_2 = 273+7 = 280\ \text{K}$

$T_1 = ?$

$\eta_1 = 0{\cdot}5$

$$\eta_1 = 1-\left(\frac{T_2}{T_1}\right)$$

$$0{\cdot}5 = 1-\left(\frac{280}{T_1}\right)$$

$$T_1 = 560\ \text{K}$$

In the second case,

$\eta_2 = 0{\cdot}7$

$$0{\cdot}7 = \left[1-\left(\frac{T_2}{T'_1}\right)\right]$$

$$T'_1 = \frac{T_2}{0{\cdot}3} = \frac{280}{0{\cdot}3} = 933{\cdot}3\text{K}$$

The increase in temperature of the source,

$$= 933{,}3-560 = \mathbf{373{\cdot}3\ K = 373{\cdot}3^\circ\ C}$$

Example A-37. *A black body at a temperature 6174 K emits radiation of wavelength 4700 Å with maximum energy. Calculate the temperature at which it will emit a wavelength of $1{\cdot}4\times10^{-5}$ cm with maximum energy.* [*Delhi (Hons.) 1990*]

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

$\therefore$ $\lambda_1 T_1 = \lambda_2 T_2$

$T_1 = 6174\ \text{K}$

$\lambda_1 = 4700\ \text{Å}$

$\lambda = 1{\cdot}4\times10^{-5}\ \text{cm} = 1400\ \text{Å}$

$T_2 = ?$

$$T_2 = \frac{\lambda_1 T_1}{\lambda_2} = \frac{4700\times6174}{1400} = \mathbf{20727\ K.}$$

Example A 38. *Calculate the value of Fermi energy for copper at absolute zero, given that the energy density of electrons in copper is $8{\cdot}5\times10^{28}$ electrons/m³, the Boltzmann constant $k = 1{\cdot}38\times10^{-23}$ J/K. $h = 6{\cdot}62\times10^{-34}$ J-s and $m_v = 9{\cdot}1\times10^{-31}$ kg.*

[*Delhi (Hons) 1990*]

$$E_F = \frac{h^2}{8m}\left[\left(\frac{3}{\pi}\right)\left(\frac{N}{V}\right)\right]^{2/3}$$

Here $h = 6{\cdot}62\times10^{-24}$ J.s

$m = 9{\cdot}1\times10^{-31}$ kg

$\frac{N}{V} = 8{\cdot}5\times10^{28}$ electrons/m³

$$\therefore \quad E_F = \left[\frac{(6{\cdot}62\times10^{-34})^2}{8\times9{\cdot}1\times10^{-31}}\right]\left[\frac{3\times85\times10^{28}}{3{\cdot}14}\right]^{2/3}$$

$$E_F = \mathbf{11{\cdot}46\times10^{-19}\ J}$$

$$E_F = \left(\frac{11{\cdot}46\times10^{-19}}{1{\cdot}6\times10^{-19}}\right)\text{eV} = \mathbf{7{\cdot}163\ eV}$$

Example A 39. *A Carnot engine has its source at 100°C and its sink is maintained at a constant temperature by means of ice at 0°C. If it is working at the rate of 100 watts, how much ice will melt in one minute ?* [*Delhi, 1991*]

$P = 100$ watts $= 100$ J/s

Work done in one minute $= 100\times60 = 6000$ J

$T_1 = 100°\text{C} = 373\ \text{K}$

$T_2 = 0°\text{C} = 273\ \text{K}$

$$\frac{H_1-H_2}{H_2} = \frac{T_1-T_2}{T_1}$$

$$\frac{W}{H_1} = \frac{T_1-T_2}{T_1} \qquad \ldots(i)$$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \qquad \ldots(ii)$$

From (i) and (ii)

$$\frac{W}{H_2} = \frac{T_1-T_2}{T_2}$$

$$H_2 = \left[\frac{WT_2}{T_1-T_2}\right] = \frac{6000\times272}{100}$$

$$H_2 = 16380\ \text{J}$$

Suppose, m kg of ice melts

$$H_2 = mL$$

$$m = \frac{H_2}{L_1} = \frac{16380}{80\times10^3\times4{\cdot}2} = \mathbf{0{\cdot}04875\ kg}$$

Example A-40. *If the RMS speed of molecules of hydrogen at NTP is 1·84 km/s, calculate the RMS speed of oxygen at NTP. The molecular weight of hydrogen and oxygen are 2 and 32 respectively.* [*Delhi. 1991*]

Here $C_1 = 1{\cdot}84$ km/s

$C_2 = ?$

$$\frac{\rho_1}{\rho_2} = \frac{2}{32} = \frac{1}{16}$$

$$\frac{C_2}{C_1} = \sqrt{\frac{\rho_1}{\rho_2}}$$

$$\frac{C_2}{1{\cdot}84} = \sqrt{\frac{1}{16}}$$

$$C_2 = \frac{1{\cdot}84}{4}$$

$$C_2 = 0{\cdot}46 \text{ km/s} = \mathbf{460 \text{ m/s}}.$$

Example A-41. *Water boils at a temperature of 101°C at a pressure of 787 mm of Hg, 1 gram of water occupies 1601 cm³ on evaporation. Calculate the latent heat of steam.* [$J = 4{\cdot}42 \times 10^7$ *ergs/cal*] [*Delhi (Hons) 1991*]

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$dP = 787 - 760 = 27$ mm of Hg

$= 2{\cdot}7$ cm of Hg

$= 2{\cdot}7 \times 13{\cdot}6 \times 980$ dynes/cm²

$dT = 1°C = 1$ K

$T = 373$ K

$V_2 - V_1 = 1601 - 1 = 1600$ cm³

$L = ?$

$$L = \frac{TdP[V_2 - V_1]}{dT}$$

$$= \frac{373 \times 2{\cdot}7 \times 13{\cdot}6 \times 980 \times 1600}{1} \text{ ergs/g}$$

$$= \mathbf{2147{\cdot}6 \times 10^7} \text{ ergs/g}$$

$$L = \frac{2147{\cdot}6 \times 10^7}{4{\cdot}2 \times 10^7} = \mathbf{511{\cdot}33 \text{ cal/g}}$$

Example A-42. *Calculate the Fermi energy and the pressure of electrons in aluminium at absolute zero.*

Density of Al $= 7{\cdot}7 \times 10^3$ *kg/m³*

Atomic weight of Al $= 27$ *kg/k mole*

$m_e = 9{\cdot}11 \times 10^{-31}$ *kg*

$k = 6{\cdot}63 \times 10^{-34}$ *J-s*

[*Delhi (Hons) 1991*]

Taking one free electron per atom, 27 kg of *Al* contains $6{\cdot}023 \times 10^{28}$ free electrons.

Density of copper $= 7{\cdot}7 \times 10^3$ kg/m³

$$V = \frac{27}{7{\cdot}7 \times 10^3}$$

$$\therefore \quad \frac{N}{V} = \frac{6{\cdot}023 \times 10^{26} \times 7{\cdot}7 \times 10^3}{27} = 1{\cdot}7177 \times 10^{29}$$

$$E_F = \frac{h^2}{8m}\left[\left(\frac{3}{\pi}\right)\left(\frac{N}{V}\right)\right]^{2/3}$$

$$E_F = \left[\frac{(6{\cdot}63 \times 10^{-34})^2}{8 \times 9\,11 \times 10^{-31}}\right]\left[\frac{3 \times 1{\cdot}7177 \times 10^{29}}{3{\cdot}14}\right]^{2/3}$$

$$E_F = \mathbf{18{\cdot}1 \times 10^{-19}\ J}$$

$$E_F = \frac{18{\cdot}1 \times 10^{-19}}{1{\cdot}6 \times 10^{-19}}$$

$$E_F = \mathbf{11{\cdot}31\ eV}$$

Pressure, $$p = \frac{2U}{3V} = \frac{2NE_F}{3V} = \left(\frac{2}{3}\right)\left(\frac{N}{V}\right)E_F$$

$$a = \frac{2}{3} \times 171{\cdot}77 \times 10^{27} \times 18{\cdot}1 \times 10^{-19}$$

$$a = \mathbf{20\,73 \times 10^{10}\ N/m^2}$$

Example A-43. *An unclothed boy is in a room at 20°C. If the skin temperature of the boy is 37°C, how much heat is lost from his body in 10 minutes. The surface area of the student is 3 m² and emissivity is 0·90 and*

$\sigma = 5{\cdot}67 \times 10^{-8}\ W/m^2 - k^4$

Here $e = 0{\cdot}9$

$A = 3\ m^2$

$\sigma = 5{\cdot}67 \times 10^{-8}\ W/m^2 - k^4$

$\theta_1 = 273 + 37 = 310$ K

$\theta_2 = 273 + 20 = 293$ K

$R = eA\,\sigma\,(\theta_1^4 - \theta_2^4)$

$R = 0{\cdot}9 \times 3 \times 5{\cdot}67 \times 10^{-8}\,[(310)^4 - (293)^4]$

$R = \mathbf{286\ J/s}$

$t = 10$ minutes $= 600$ s

Total heat lost by the skin in 10 minutes.

$$Q = Rt = 286 \times 600 = \mathbf{1{\cdot}716 \times 10^5\ J}$$

Example A-44. *Air in the cylinder of a combustion engine at 20°C is compressed from an initial pressure of 1 atmosphere and volume* 8×10^{-4} *m³ to a volume* 6×10^{-5} *m³. Assume that air behaves an ideal gas* ($\gamma = 1{\cdot}40$) *and the process is adiabatic, calculate*

(*a*) *final pressure* (*b*) *final temperature of the gas*

Process is adiabatic

(a) $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$$P_2 = P_1\left[\frac{V_1}{V_2}\right]^{\gamma}$$

Here $P_1 = 1$ atmosphere

$V_1 = 8\times10^{-4}\ m^3$

$V_2 = 6\times10^{-5}\ m^3$

$T_1 = 273+20 = 293\ K$

$$P_2 = 1\left[\frac{8\times10^{-4}}{6\times10^{-5}}\right]^{1.4}$$

$P_2 = 37{\cdot}6$ atmospheres

(b) Since $\frac{PV}{T}$ is always constant during the process as ne gas has escaped from the cylinder

$$\frac{PV}{T} = nR = \text{constant}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$T_2 = \left(\frac{P_2}{P_1}\right)\left(\frac{V_2}{V_1}\right)T_1$$

$$T_2 = \left(\frac{37{\cdot}6}{1}\right)\left(\frac{6\times10^{-5}}{8\times10^{-4}}\right)293$$

$T_2 = 826{\cdot}2$ K

$T_2 = 553{\cdot}2°C$

Example A-45. *A point source of Power P is placed at the centre of a spherical shell of mean radius R. The material of the shell has thermal conductivity K. If the temperature difference between the outer and inner surface of the shell is not to exceed T, the thickness of the shell should not be less than.....*

[J. I. T. Entrance Exam, 1991]

Here $\frac{dQ}{dt} = P = KA\left(\frac{dT}{dr}\right)$

$$\frac{dQ}{dt} = K(4\pi r^2)\ \frac{dT}{dr} = P$$

$$\therefore \quad \frac{dr}{r^2} = \left(\frac{4\pi K}{P}\right)dT$$

Integrating

$$\int_{r_1}^{r_2}\frac{dr}{r^2} = \frac{4\pi K}{P}\int dT$$

$$\frac{1}{r_1}-\frac{1}{r_2} = \frac{4\pi KT}{P}$$

$$(r_2-r_1) = \left(\frac{4\pi KT}{P}\right)r_1r_2$$

Approximately $r_1 \simeq r_2 \sim R$, $\because\ r_1r_2 = R^2$

$$(r_2-r_1) = \left(\frac{4\pi KT}{P}\right)R^2$$

Example A-46 *A solid copper sphere (density ρ and specific heat C) of radius r at initial temperature 200 K is suspended inside a chamber whose walls are at almost OK. The time required for the temperature of the sphere to fall to 100 K is.....*

[I.I.T. Entrance Exam, 1991]

Here $\frac{dQ}{dt} = e\sigma A(T_s^4-T_0^4)$

Here $e = 1$

and $A = 4\pi r^2$

Also $\frac{dQ}{dt} = mc\left(\frac{dT}{dt}\right)$

Also $m = \left(\frac{4}{3}\pi r^3\right)\rho$

$$\therefore \quad mc\left(\frac{dT}{dt}\right) = \sigma A(T^4-T_0^4)$$

$T_0 = 0$

$$dt = \left(\frac{m}{A}\right)\left(\frac{C}{\sigma}\right)\frac{dT}{T^4}$$

Integrating

$$\int dt = \left(\frac{\frac{4}{3}\pi r^3\rho}{4\pi r^2}\right)\left(\frac{C}{\sigma}\right)\int_{200}^{100}\frac{dT}{T^4}$$

$$t = \left(\frac{r\rho C}{3\sigma}\right)\left(\frac{1}{3}\right)\left[\left(\frac{1}{200}\right)^3-\left(\frac{1}{100}\right)^3\right]$$

$$t = \left[\frac{7r\rho C}{(72\times10^6)\sigma}\right]$$

Example A-47. *The molecular diameter of an ideal gas is 2×10^{-10} m at a temperature of 20°C and pressare 1 atmosphere. Calculate the*

(a) mean free path

(b) collision frequency

Velocity of molecules at

20°C = 511 m/s,

Take I atmospheric pre-sure

$= 1{\cdot}01\times10^5\ N/m^2$

(a) Here $T = 293$ K

As the gas is ideal, the equation

$$PV = N k T \text{ can be applied}$$

$$\therefore \quad n = \frac{N}{V} = \frac{P}{kT} = \frac{1{\cdot}01\times10^{5}}{(1{\cdot}38\times10^{-23})\times 293}$$

$$n = 2{\cdot}5\times10^{25} \text{ molecules/m}^3$$

mean free path,

$$\lambda = \frac{1}{1{\cdot}414\times\pi\, d^2 n}$$

$$\lambda = \frac{1}{1{\cdot}414\times\pi\,(2\times10^{-10})^2\times(2{\cdot}5\times10^{25})}$$

$$\lambda = 2{\cdot}25\times10^{-7} \text{ m}$$

(*b*) collision frequency

$$f = \frac{\bar{v}}{\lambda} = \frac{511}{2{\cdot}25\times10^{-7}}$$

$$f = 2{\cdot}27\times10^{9} \text{ per second}$$

Example A-48. *Calculate the number of collisions per second of c molecule of a gas having mean free path $1{\cdot}876\times10^{-7}$ m. Take average speeh of the molecule as 511 m/s.* [*Delhi 1992*]

Mean free path $\lambda = 1{\cdot}876\times10^{-7}$ m

$v = 511$ m/s

Collision frequency,

$$f = \frac{\bar{v}}{\lambda} = \frac{511}{1{\cdot}876\times10^{-7}} = 2{\cdot}72\times10^{9} \text{ per second}$$

Example A-49. *Calculate the increase in entropy of 1 kg. of ice when it is converted into steam. Given the specific heat of water is 1 k cal/kg-°C latent heat of ice is 80 kcal/kg and the latent heat of steam is 540 k cal/kg.* [*Delhi, 1992*]

(1) Increase in entropy when 1 kg of ice at 0°C is converted into water at 0°C.

$$dS = \frac{\delta H}{T} = \frac{80}{273} = 0{\cdot}293 \text{ k cal/K}$$

(2) Increase in entropy when the temperature of 1 kg of water is raised from 0°C to 100°C.

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T} = ms\times 2{\cdot}3026 \log_{10}\left(\frac{T_2}{T_1}\right)$$

$$= 1\times1\times2{\cdot}3026 \log_{10}\left(\frac{373}{273}\right) = 0{\cdot}312 \text{ k cal/K}$$

(3) Increase in entropy when 1 kg of water at 100°C is converted into steam at 100°C.

$$dS = \frac{\delta H}{T} = \frac{540}{373} = 1{\cdot}447 \text{ k cal/K}$$

Total increase in entropy,

$$dS = 0{\cdot}293 + 0{\cdot}312 + 1{\cdot}447 = 2{\cdot}052 \text{ k cal/K}.$$

Example A-50 *Calculate the rise in temperature of a gas initially at 27°C, if its pressure is suddenly doubled, $\gamma = 1.4$* [*Kerala, 1992*]

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

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

Here, $\quad P_2 = 2P_1$

$$T_1 = 27^{\circ}\text{C} = 27 + 273 \text{ K}$$

$$= 300 \text{ K}$$

$$T_2 = ?$$

$$\gamma = 1.4$$

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

$$0.4 \log 2 = 1.4\,[\log T_2 - \log 300]$$

$$0.4 \times 0.3010 = 1.4\,[\log T_2 - 2.4771]$$

$$\log T_2 = 0.086 + 2.4771$$

$$= 2.5631$$

$$T_2 = 365.7 \text{ K}$$

$$= 365.7 - 273 = 92.7^{\circ}\text{C}$$

Rise in temperature $= (92.7 - 27)\,^{\circ}\text{C}$

$$= 65.7^{\circ}\text{C}$$

Example A-51 *Calculate the work done when one litre of a monoatomic perfect gas at N.T.P. is compressed adiabatically to half its volume* $\gamma = 1.67$

[*Calicut, 1992*]

Here $\quad V_1 = 1 \text{ litre} = 10^3 \text{cm}^3 = 10^{-3}\text{m}^3$

$$V_2 = 0.5 \text{ litre} = 500 \text{ cm}^3 = 5 \times 10^{-4}\text{m}^3$$

$$\gamma = 1.67$$

Work done

$$W = \left(\frac{1}{1-\gamma}\right)\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right]$$

$$W = \left(\frac{1}{1-1.67}\right)\left[\left(\frac{1}{5\times10^{-4}}\right)^{0.67} - \left(\frac{1}{10^{-3}}\right)^{0.67}\right]$$

$$= -\left(\frac{1}{0.67}\right)\left[(2\times10^{3})^{0.67} - (10^{3})^{0.67}\right]$$

$$= -\left(\frac{1}{0.067}\right)\left[162.8 - 102.3\right]$$

$$= -90.3 \text{ J}$$

Negative sign shows, work is done on the gas.

Hence work done on the gas = **90.3 J**

Example A-52 *Two Carnot engines X and Y are operating in series. The first one X receives heat at* 1200 K *and rejects to a reservoir at temperature T* K *The second engine Y receives the heat rejected by X and inturn rejects to a heat reservoir at* 300 K *Calculate the temperature T for the situation when:*

(i) *The work outputs of two engines are equal.*

(ii) *The efficiency of two engines are equal.*

[Kanpur, 1991]

(1) When work outputs are equal.

For the first engine,

$$W_1 = H_1 - H_2$$

For the second engine,

$$W_2 = H_2 - H_3$$

Here $W_1 = W_2$

$$H_1 - H_2 = H_2 - H_3$$

$$\left(\frac{H_1}{H_2}\right) - 1 = 1 - \left(\frac{H_3}{H_2}\right)$$

Also $\frac{H_1}{H_2} = \frac{1200}{T}$ and $\frac{H_2}{H_3} = \frac{T}{300}$ or $\frac{H_3}{H_2} = \frac{300}{T}$

$$\therefore \quad \left(\frac{1200}{T}\right) - 1 = 1 - \frac{300}{T}$$

or $T = 750$ K

(2) When efficiencies are equal.

$$\eta_1 = 1 - \left(\frac{H_2}{H_1}\right)$$

$$\eta_2 = 1 - \left(\frac{H_3}{H_2}\right)$$

$$\eta_1 = \eta_2$$

$$1 - \left(\frac{H_2}{H_1}\right) = 1 - \left(\frac{H_3}{H_2}\right)$$

$$1 - \left(\frac{T}{1200}\right) = 1 - \left(\frac{300}{T}\right)$$

$$\frac{T}{1200} = \frac{300}{T}$$

$$T = 600 \text{ K}$$

Example A-53 *A Carnot engine working between a source at temperature* 27°C *and a sink at* –73°C *delivers 300 calories of heat to the latter in one cycle. Calculate the work performed in joules by the engine per cycle.*

[Calcutta, 1992]

Here, $T_1 = 27 + 273 = 300$ K

$T_2 = -73 + 273 = 200$ K

$H_2 = 300$ calories.

$H_1 = ?$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$\frac{H_1}{300} = \frac{300}{200}$$

$H_1 = 450$ calories

Work performed per cycle,

$$W = H_1 - H_2$$

$$= 450 - 300$$

$$= 150 \text{ calories}$$

$$= 150 \times 4.2 \text{ J}$$

$$= 630 \text{ J}$$

Example A-54 *In a cold storage ice melts at the rate of 3 kg. per hour when the external temperature is* 28°C. *Find the minimum power output of the motor used to run the refrigerator just to prevent melting of ice.*

Specific latent heat of ice fusion $= 3.3 \times 10^5 \text{ J kg}^{-1}$

[Calicut, 1992]

$m = 3$ kg

$L = 3.3 \times 10^5$ J kg^{-1}

$s = 4.2 \times 10^3 = $ J kg^{-1} – °C

Heat taken by ice to melt into water and reach a temperature of 28°C in one hour.

$$Q = mL + ms\theta$$
$$= 3 \times 3.33 \times 10^5 + 3 \times 4.2 \times 10^3 \times 28$$
$$= 1.343 \times 10^6 \text{ J}$$

To prevent melting of ice, the refrigerator should have the power out,

$$P = 1.343 \times 10^6 \text{ J/hour}$$
$$= \frac{1.343 \times 10^6}{3600} \text{ J/s}$$
$$= 373 \text{ Watts.}$$

Example A-55 *Calculate the depression of melting point of ice by one atmosphere increase of pressure, given, latent heat of ice* $= 3.35 \times 10^5$ J/kg *and the specific volumes of 1 kg. of ice and water at* 0°C *are* 1.090×10^{-3} m^3 *and* 10^{-3} m^3 *respectively.*

[*Kerala, 1992*]

Here, $L = 3.35 \times 10^5$ J/kg

$T = 273$ K

$V_1 = 1.090 \times 10^{-3}$ m^3

$V_2 = 10^{-3}$ m^3

$dP = 1$ atmosphere

$= 0.76 \times 13.6 \times 10^3 \times 9.8$

$= 1.01 \times 10^5$ N/m^2

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$$dT = \frac{dP \times T\,[V_2 - V_1]}{L}$$

$$= \frac{1.01 \times 10^5 \times 273\,[10^{-3} - 1.09 \times 10^{-3}]}{3.35 \times 10^5}$$

$$= -7.4 \times 10^{-3} \text{ K}$$

$$= -7.4 \times 10^{-3} \text{ °C}$$

Therefore, decrease in melting point of ice with an increase in pressure of one atmosphere

$$= 7.4 \times 10^{-3} \text{ K} = 7.4 \times 10^{-3} \text{ °C}$$

Example A-56 *Find the change in boiling point of water for* 100 cm *change in mercury pressure if the specific volume of steam is* 1601 cm^3/gram *at* 100°C *and* 76 cm *mercury pressure. Take latent heat as* 536 cal/gram.

[*Allahabad, 1992*]

[In SI system],

Here $dP = 100$ cm Hg $= 1$ m Hg

$= 1 \times 13.6 \times 10^3 \times 9.8$ N/m^2

$= 1.33 \times 10^5$ N/m^2

$V_1 = 1$ cm^3/gram $= 10^{-3}$ m^3/kg

$V_2 = 1601$ cm^3/gram $= 1601 \times 10^{-3}$ m^3/kg

$L = 536$ cal/gram

$= 536 \times 4.2 \times 10^3$ J/kg

$= 2.25 \times 10^6$ J/kg

$T = 100$°C $= 373$ K

$dT = ?$

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$$dT = \frac{dP \times T\,[V_2 - V_1]}{L}$$

$$= \frac{1.33 \times 10^5 \times 373\,[1601 \times 10^{-3} - 10^{-3}]}{2.25 \times 10^6}$$

$$= 35.28 \text{ K}$$

$$= 35.28 \text{°C}$$

Therefore, increase in boiling point of water with an increase of 100 cm in mercury pressure

$$= 35.28 \text{ K} = 35.28 \text{°C}$$

Example A-57 *The ratio of the densities of ice and water at* 0°C *is* $\frac{10}{11}$. *Calculate the decrease in the melting point of ice, given that latent heat of fusion of ice* $= 80$ *cal/gm and change in specific volume* -0.1 c.c./gm. *The increase in pressure is one atmosphere.*

[*Osmania, 1992*]

[In SI system],

$dP = 0.76 \times 13.6 \times 10^3 \times 9.8 = 1.01 \times 10^5$ N/m^2

$$L = 80 \text{ cal/gram}$$

$$= 80 \times 4.2\ 10^3 \text{ J/kg}$$

$$= 3.36 \times 10^5 \text{ J/kg}$$

$$T = 273 \text{ K}$$

$$V_2 - V_1 = -0.1 \text{ cm}^3\text{/gram}$$

$$= -0.1 \times 10^{-3} \text{ m}^3\text{/kg}$$

$$dT = ?$$

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$$dT = \frac{dP \times T\,[V_2 - V_1]}{L}$$

$$= \frac{1.01 \times 10^5 \times 273\,[-0.1 \times 10^{-3}]}{3.36 \times 10^5}$$

$$= -8.2 \times 10^{-3} \text{ K}$$

$$= -8.2 \times 10^{-3} \text{ °C}$$

Therefore, the decrease in the melting point of ice with an increase in pressure of one atmosphere.

$$= 8.2 \times 10^{-3} \text{ K} = 8.2 \times 10^{-3} \text{ °C}$$

Example A-58 *Calculate the change of entropy on converting a mole of a gas occupying 20 litres at a pressure of* 2×10^5 N/m^2 *to occupying 50 litres at a pressure of* 5×10^5 N/m^2. *Given*

$R = 8.4$ J mol^{-1} K^{-1}

$C_v = 21$ J mol^{-1} K^{-1}

[*Kerala, 1992*]

Here, $P_1 = 2 \times 10^5$ N/m^2

$V_1 = 20$ litres

$P_2 = 5 \times 10^5$ N/m^2

$V_2 = 50$ litres

For a perfect gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

$$= \frac{5 \times 10^5 \times 50}{2 \times 10^5 \times 20}$$

$$= 6.25$$

Also, $\frac{V_2}{V_1} = \frac{50}{25} = 2.5$

$$C_v = 21 \text{ J/mol - K}$$

$$R = 8.4 \text{ J/mol - K}$$

The change in entropy,

$$dS = C_v \times 2.3026 \log_{10}\left(\frac{T_2}{T_1}\right) + R \times 2.3026 \log_{10}\left(\frac{V_2}{V_1}\right)$$

$$= 21 \times 2.3026 \log_{10}(6.25) + 8.4 \times 2.3026 \log_{10}(2.5)$$

$$= 21 \times 2.3026 \times 0.7959 + 8.4 \times 2.3026 \times 0.3979$$

$$= 38.4852 + 7.6961$$

$$= 46.1813$$

$$= 46.18 \text{ J/K}$$

Therefore, increase in entropy = **46.18 J / K**

Example A-59 *Assuming the specific heat capacity of water, find the change in entropy when 0.1 kg. of water at* 15°C *is mixed with 0.16 kg. of water at* 40°C

[*Calicut, 1992*]

[In SI system],

Specific heat of water,

$$s = 1 \text{ k cal/ kg - °C}$$

$$= 4.2 \times 10^3 \text{ J/ kg - °C}$$

Here, $m_1 = 0.1$ kg

$T_1 = 15 + 273 = 288$ K

$m_2 = 0.16$ kg

$T_2 = 40 + 273 = 313$ K

Let the final temperature be T

$$m_1 \times s \times [T - T_1] = m_2 \times s \times [T_2 - T]$$

$$m_1 [T - T_1] = m_2 [T_2 - T]$$

$$0.1\,[T - 288] = 0.16\,[313 - T]$$

$$T = 303.4 \text{ K}$$

(i) Change in entropy when the temperature of 0.1 kg of water rises from 288 K to 303.4 K

$$\frac{\delta H}{T} = m s \int_{T_1}^{T} \left(\frac{dT}{T}\right)$$

$$= 0.1 \times 4.2 \times 10^3 \times 2.3026 \log_{10} \left(\frac{303.4}{288}\right)$$

$$= \mathbf{21.88\ J/K}$$

(ii) Change in entropy when the temperature of 0.16 kg of water decreases from 313 K to 303.4 K

$$\frac{\delta H}{T} = m s \int_{T_2}^{T} \left(\frac{dT}{T}\right)$$

$$= 0.16 \times 4.2 \times 10^3 \times 2.3026 \log_{10} \left(\frac{303.4}{313}\right)$$

$$= -20.93\ \text{J/K}$$

Therefore, the net change in entropy of the system = + 21.88 − 20.93

$$= \mathbf{0.95\ J/K}$$

Hence, net increase in entropy,

$$= \mathbf{0.95\ J/K}$$

Example A-60 *12.5 gm of ice at* −24°C *is converted into steam at* 100°C *Calculate the change in entropy. It is given that, latent heat of steam = 5.36 cal/gm, latent heat of ice = 80 cal/gm. specific heat of ice = 0.5 cal/gm-K.*

[Bhagalpur, 1992]

[In SI system],

m = 12.5 grams = 12.5×10^{-3} kg

Latent heat of ice = 80 cal/gram = $80 \times 10^3 \times 4.2$ J/ kg

$= 3.36 \times 10^5$ J/ kg

Latent heat of steam = 536 cal/gram = 536×10^3 4.2 J/ kg

$= 2.25 \times 10^6$ J/ kg

Specific heat of ice = 0.5 cal/gram − K

$= 0.5 \times 10^3 \times 4.2$ J/ kg − K

$= 2.1 \times 10^3$ J/ kg − K

Specific heat water = 1 cal/gram − K

$= 1 \times 10^3\ 4.2 \times$ J/ kg − K

$= 4.2 \times 10^3$ J/ kg − K

(1) Increase in entropy when temperature of 12.5×10^{-3} kg of ice is increased from −24°C to 0°C (249 K to 273 K)

$$dS = \int_{T_2}^{T_1} \frac{\delta H}{T}$$

$$= m s \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= m s \log_e \left(\frac{T_2}{T_1}\right)$$

$$= 12.5 \times 10^{-3} \times 2.1 \times 10^3 \log_e \left(\frac{273}{249}\right)$$

$$= 12.5 \times 2.1 \times 2.3026 \log_{10} \left(\frac{273}{249}\right)$$

$$= \mathbf{2.42\ J/K}$$

(2) Increase in entropy when 12.5×10^{-3} kg of ice at 0°C is converted into water at 0°C

$$dS = \frac{\delta H}{T} = \frac{m L}{T}$$

$$= \frac{12.5 \times 10^{-3} \times 3.36 \times 10^5}{273}$$

$$= \mathbf{15.38\ J/K}$$

(3) Increase in entropy when the temperature of 12.5×10^{-3} kg of water is raised from 0°C to 100°C (273 K to 373 K)

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= m s \times 2.3026 \log_{10} \left(\frac{T_2}{T_1}\right)$$

$$= 12.5 \times 10^{-3} \times 4.2 \times 10^3 \times 2.3026 \log_{10} \left(\frac{373}{273}\right)$$

$$= \textbf{16.38 J/K}$$

(4) Increase in entropy when 12.5×10^{-3} kg of water at 100°C is converted into steam at 100°C (373 K)

$$dS = \frac{\delta H}{T} = \frac{mL}{T}$$

$$= \frac{12.5 \times 10^{-3} \times 2.25 \times 10^{6}}{373}$$

$$= \textbf{75.4 J/K}$$

Total increase in entropy

$$= 2.42 + 15.38 + 16.38 + 75.4$$

$$= \textbf{109.58 J/K}$$

Example A-61 *How much time will it take for a layer of ice of thickness 20 cm to increase by 10 cm, on the surface of a pond, when the temperature of surroundings is −15°C ?*

K = 0.005 C.G.S; units; L = 80 Cal/g, ρ = 0.90 g/cm³

[Kanpur, 1991]

[In CGS system],

$$\int dt = \frac{\rho L}{K\theta} \int x\, dx$$

$$t = \frac{\rho L}{2K\theta}\left[x_2^2 - x_1^2\right]$$

Here, $\rho = 0.9$ g/cm³

$L = 80$ cal/cm³

$K = 0.005$ C G S units

$\theta = 15°C$

$x_1 = 20$ cm

$x_2 = 30$ cm

$$t = \left[\frac{0.9 \times 80}{2 \times 0.005 \times 15}\right]\left[(30)^2 - (20)^2\right]$$

$$= 2.4 \times 10^5 \text{ s}$$

$$= \textbf{66 hrs – 40 min}$$

Example A-62 *A solid copper sphere of radius R is at a temperature of 121°C and it cools at a rate of 2.6°C per minute. At what rate a solid copper sphere of radius 2R will cool when kept at a temperature of 195°C ? If in both the cases the surroundings are maintained at 30°C and Stefan's law is applicable.*

[Bhagalpur, 1992]

Here, $\frac{d\theta_1}{dt} = 2.6°C$ per minute

Energy radiated per minute,

$$E_1 = m_1 s\left(\frac{d\theta_1}{dt}\right)$$

For first sphere,

$$m_1 = \left(\frac{4}{3}\pi R_1^3 S\right)$$

$$\frac{d\theta_1}{dt} = 2.6°C \text{ per minute}$$

Also, $E_1 = A_1 e \sigma t\left(T_1^4 - T_0^4\right)$

Here, $T_1 = 273 + 121 = 394$ K

$T_0 = 273 + 30 = 303$ K

$A_1 = 4\pi R_1^2$

Similarly, for the second sphere,

$$E_2 = m_2 s\left(\frac{d\theta_2}{dt}\right)$$

$$E_2 = A_2 e \sigma t\left(T_2^4 - T_0^4\right)$$

Here, $A_2 = 4\pi R_2^2$

and $m_2 = \frac{4}{3}\pi R_2^3$

$T_2 = 273 + 195 = 468$ K

$$\therefore\ m_1 s\left(\frac{d\theta_1}{dt}\right) = A_1 e \sigma t\left(T_1^4 - T_0^4\right) \quad \ldots.(i)$$

and $$m_2 s\left(\frac{d\theta_2}{dt}\right) = A_2 e \sigma t\left(T_2^4 - T_0^4\right) \quad \ldots.(ii)$$

Dividing (ii) by (i),

$$\left(\frac{m_2}{m_1}\right)\left[\frac{\left(\frac{d\theta_2}{dt}\right)}{\left(\frac{d\theta_1}{dt}\right)}\right] = \left(\frac{A_2}{A_1}\right)\left[\frac{T_2^4 - T_0^4}{T_1^4 - T_0^4}\right]$$

$$\left(\frac{\frac{4}{3}\pi R_2^3}{\frac{4}{3}\pi R_1^3}\right)\left(\frac{\frac{d\theta_2}{dt}}{2.6}\right) = \left(\frac{4\pi R_2^2}{4\pi R_1^2}\right)\left[\frac{(468)^4 - (303)^4}{(394)^4 - (303)^4}\right]$$

$$\left(\frac{d\theta_2}{dt}\right) = (2.6)\left(\frac{R_1}{R_2}\right)\left[\frac{(4.8 \times 10^{10}) - (0.84 \times 10^{10})}{(2.41 \times 10^{10}) - (0.84 \times 10^{10})}\right]$$

But $R_2 = 2\,R_1$

$$\therefore \quad \frac{d\theta_2}{dt} = 2.6\left(\frac{1}{2}\right)(2.52)$$

$$= \mathbf{3.276^\circ C \text{ per minute}}$$

Example A-63 *The temperature gradient of an insulated copper rod is* 250°C/metre. *Compute the difference in temperature between two points separated by 0.05 m. Determine the amount of heat crossing per second per unit area normal to the rod. Given thermal conductivity of copper is* $384\ W\ m^{-1}\ K^{-1}$

[*Kerala, 1992*]

(i) Here, $\frac{d\theta}{dx} = 250^\circ C/m$

For $x = 0.05\ m$

Temperature difference,

$$(\theta_1 - \theta_2) = 250 \times 0.05$$

$$= \mathbf{12.5^\circ C}$$

(ii) $$Q = KA\left(\frac{d\theta}{dx}\right)t$$

For $t = 1$ second

$K = 384\ W/m - K$

$A = 1\ m^2$

$$\frac{d\theta}{dx} = 250^\circ C/m = 250\ K/m$$

$$Q = 384 \times 1\ (250)\ 1$$

$$Q = \mathbf{9.6 \times 10^4\ J/s.}$$

Example A-64 *Compare the radiant emittance of a black body at 200 K and 2000 K. Given* $\sigma = 5.672 \times 10^{-8}$ M. K. S. *units.*

[*Kerala, 1992*]

Here, $T_1 = 200\ K$

$T_2 = 2000\ K$

$R_1 = \sigma\ T_1^4$

$R_2 = \sigma\ T_2^4$

$$\left(\frac{R_1}{R_2}\right) = \left(\frac{T_1}{T_2}\right)^4$$

$$= \left(\frac{200}{2000}\right)^4$$

$$= \mathbf{10^{-4}}$$

Example A-65 *A black sphere of diameter 8 cm. is heated to 500 K when the surrounding temperature is 300 K. What is the rate at which energy is radiated ? Stefan's constant* $x6 \times 10^{-8}\ W\ m^{-2}\ K^{-4}$

[*Calicut, 1992*]

Here, $\sigma = 6 \times 10^{-8}\ W\ m^{-2}\ K^{-4}$

$t = 1\ s$

$T = 500\ K$

$T_0 = 300\ K$

$d = 8\ cm = 0.08\ m$

$A = \pi d^2$

$= 3.14 \times (0.08)^2$

$= 0.02\ m^2$

$e = 1$

$R = \sigma A e\left[T^4 - T_0^4\right]$

$= 6 \times 10^{-8} \times 0.02 \times 1\left[(500)^4 - (300)^4\right]$

$= \mathbf{65.28\ J/s}$

$= \mathbf{65.28\ watts}$