HEAT
AND
THERMODYNAMICS

[For B.Sc. (Pass, General Subsidiary), B.Sc. (Hons. and Engineering) and Medical and Engineering colleges Entrance, IAS Examinations]

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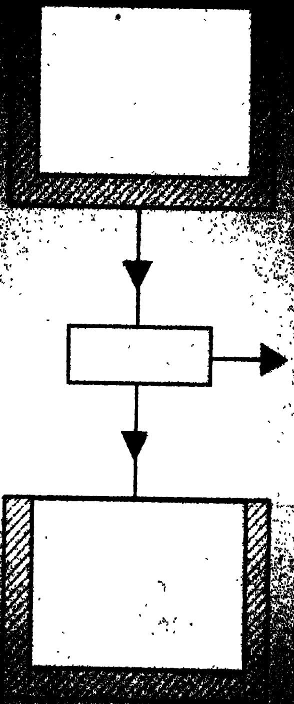

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PREFACE TO THE SIXTEENTH EDITION

The present edition of the book has been revised. A new Chapter on Statistical Thermodynamics is included in this edition. This chapter deals with Statistical Equilibrium, Maxwell Boltzmann Distribution, Fermi-Dirac Distribution and Bose-Einstein Distribution. The statistical behaviour of an ideal gas, an electron gas and a photon gas has also been discussed and the comparison of the three statistics is discussed.

The whole chapter on thermodynamics is thoroughly reoriented. The following new topics have been added :

1. Richardson's equation 2. Reversible and irreversible processes. 3. Gibb's function. 4. Helmholtz function. 5. Enthalpy. 6. First order phase transitions. 7. Second order phase transitions. 8. Theory of adiabatic demagnetisation. 9. Maxwell's thermo-dynamical relations. 10. Properties of matter near critical point. 11. *T-ds* equation. 12. Heat and Work as path functions. 13. Quasi-static process. 14. Gibb's phase rule. 15. Joule-Kelvin coefficient 16. C_p, C_v and μ.

A few new topics have been included in the Appendix at the end of the book.

Temperatures on the thermodynamic scale are denoted as *T* and the unit used is Kelvin (Symbol K). It may be noted that the symbol in SI units is K and not °K.

The exercises at the end of each chapter are brought up-to-date and questions from recent university papers have been added. We are grateful to the students and teachers for the favourable response given to the book. Suggestions for further improvement of the book will be highly appreciated. Our grateful thanks are due to Shri R.K. Gupta for printing the book in time.

BRIJ LAL

DELHI N. SUBRAHMANYAM

PREFACE TO THE FIRST EDITION

This book on "Heat and Thermodynamics" is primarily intended for students preparing for degree examinations of Indian Universities.

The subject matter is divided into eight chapters. Much of the elementary material with which the students are already familiar at the higher secondary level is not included. The material is presented in a comprehensive way and the sequence of articles in each chapter enables the students to understand the development of the subject.

The chapter on thermodynamics includes a large number of topics *viz,* zeroth law of thermodynamics, concept of heat, problems concerning entropy, Maxwell's thermodynamical relations, the first, the second and the third laws of thermodynamics, practical working of heat engines, refrigerators and the concept of negative temperatures. Based on the syllabus for degree classes of different universities, equal emphasis is also given to chapters concerning thermometry, specific heat, kinetic theory, liquefaction of gases, production of low temperatures, pyrometry and transmission of heat.

A large number of diagrams to illustrate the basic principles are given in the book. Solved numercial examples are also given at the end of each chapter to enable the students to apply the formulae and principles studied. The exercises at the end of each chapter contain a large number of questions including numerical problems and these are mainly selected from question papers of different Universities.

We are greatly indebted to Prof. Y.V.S.R. Sastry, M.E., Ph.D., Professor of Mechanical Engineering, Delhi College of Engineering, Delhi, for his valuable help in reading and suggesting improvements in the chapter on thermodynamics. We are also thankful to Mr. Raj Kumar Seth, Sales Manager and P.N. Kapoor for the interest they took in getting the book published.

We hope that this book will be found useful by the students and teachers in the various institutions in India. We will appreciate any suggestions for the improvement of the book.

BRIJ LAL
N. SUBRAHMANYAM

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STATISTICAL THERMODYNAMICS

Appendix I

Appendix II

1

Thermometry

1·1 Concept of Heat and Temperature

It is not possible to speak of work in a body. Similarly, it is not possible to speak of heat in a body. Work is either done on a body or by a body. Similarly, heat can flow from a body or to a body. If a body is at a constant temperature, it has both mechanical and thermal energies due to the molecular agitation and it is not possible to separate them. So, in this case, we cannot talk of heat energy. It means, if the flow of heat stops, the word heat cannot be used. It is only used when there is transfer of energy between two or more systems. Therefore, heat can be defined as ***energy in transit.***

Temperature of a system can be defined as the property that determines whether or not the body is in thermal equilibrium with the neighbouring systems. If a number of systems are in thermal equilibrium, this common property of the system can be represented by a single numerical value called the temperature. It means that if two systems are not in thermal equilibrium, they are at different temperatures.

Example. In a mercury in glass thermometer the pressure above the mercury column is zero and volume of mercury measures the temperature. If a thermometer shows a constant reading in two systems A and B separately, it will show the same reading even when A and B are brought in contact.

Measurement of temperature of a body accurately is one of the important branches of heat in physics. It also becomes necessary to measure high temperatures and low temperatures. To make this measurement possible, it is necessary to construct a suitable scale of temperature. The scale chosen must be precise and consistent and the temperatures measured on this scale must be accurate. Assessing the temperature of a body by mere sense of touch or comparing the degree of hotness of a body with respect to another body does not help in measuring the temperature quantitatively and accurately.

1·2 Thermometry

The branch of heat relating to the measurement of temperature of a body is called *thermometry*. Thermometer is an instrument used to measure the temperature of a body.

The essential requisites of a thermometer are :

(1) Construction,
(2) Calibration, and
(3) Sensitiveness.

(1) *Construction.* The physical property of a substance plays an important role in the construction of a thermometer. In a mercury thermometer, the principle of expansion of mercury with rise in temperature is used. The platinum resistance thermometer is based on the principle of the change in resistance with change in temperature. The gas thermometer is based on the principle of change in volume or pressure with change in temperature. Thus, for the construction of a thermometer, the proper choice of a substance, whose physical property varies uniformly with rise in temperature, is essential.

(2) *Calibration.* When a thermometer is constructed, it should be properly calibrated. The standard fixed points are selected for calibrating a thermometer. Melting point of ice, boiling point of water, melting point of silver and melting point of gold are taken as fixed points. The scales are built by dividing the interval between the two fixed points into equal parts. Centigrade scale is built by dividing the interval between the melting point of ice and the boiling point of water (under normal pressure) into 100 equal parts and each part represents 1°C. Similarly, Fahrenheit scale is built by dividing this interval into 180 equal parts

(3) *Sensitiveness.* The instrument, once constructed and calibrated, should also be sensitive. The thermometer will be sensitive if (*i*) it can detect even small changes in temperature, (*ii*) it shows the temperature of a body in a short time and (*iii*) it does not take large quantity of heat for its own heating from the body whose temperature is being measured.

Fixed points	*Degrees Celsius*
Boiling point of oxygen	—182·97
Ice point	0·00
Steam point	100·00
Boiling point of sulphur	444·60
Melting point of silver	960·80
Melting point of gold	1063·00
Melting point of cobalt	1492·00
Melting point of platinum	1769·00
Melting point of rhodium	1960·00
Melting point of tungsten	3380.00

1·3 Types of Thermometers

There are different kinds of thermometers :

(1) *Liquid thermometers.* These thermometers are based on the principle of change in volume of a liquid with change in temperature. Mercury and alcohol thermometers are based on this principle.

(2) *Gas thermometers.* These are based on the principle of change in pressure or volume with change in temperature, *e.g.*, Callendar's constant pressure thermometer, constant volume hydrogen thermometer etc.

(3) *Resistance thermometers.* These are based on the principle of change in resistance with change in temperature, *e.g.*, platinum resistance thermometer.

(4) *Thermo-electric thermometers.* These are based on the principle of thermo-electricity, *i.e.*, production of thermo-E.M.F. in a thermo-couple when the two junctions are at different temperatures.

The various thermocouples commonly used are :—

(1) Copper and constantan

(2) Iron and constantan

(3) Chromel and constantan

(4) Chromel and alumel

(5) Platinum and Rhodium.

(5) *Radiation thermometers.* These are based on the quantity of heat radiations emitted by a body *e.g.*, furnaces. These instruments are known as pyrometer.

(6) *Vapour pressure thermometers.* These are based on the principle of change of vapour pressure with change in temperature. These are used to measure low temperatures, *e.g.*, helium vapour pressure thermometer etc.

(7) *Bimetallic thermometers.* These thermometers are based on the principle of expansion of solids. A bimetallic strip is taken in the form of a spiral. Its one end is fixed and the other end is attached to a long pointer. The pointer moves on a scale, calibrated in degrees. These thermometers are used in meteorology for recording the changes in temperature during the day. They are also used to measure temperatures at high altitudes.

(8) *Magnetic thermometers.* These thermometers are based on the principle of change in the susceptibility of a substance with temperature. These thermometers are useful for measuring low temperatures near the absolute zero temperature.

1·4 Centigrade and Fahrenheit Scales

The earliest thermometer was constructed by Galileo in 1593. Newton suggested the necessity of the fixed points. The temperature of the melting point of ice is taken as the lower fixed point and the temperature of steam at a pressure of 76 cm of Hg (normal pressure) is taken as the upper fixed point.

Centigrade (or Celsius) scale. Celsius, in 1742, suggested the centigrade system of temperature. He marked zero at the lower fixed point and 100 at the upper fixed point. The interval between the two fixed points is divided into 100 equal parts. Each part or degree represents 1°C or 1° Celsius. The scale is also known as Celsius scale.

Fahrenheit scale. Fahrenheit, in 1720, suggested this scale by taking zero as the temperature of the freezing mixture. It appears that he took 100 degrees as the temperature of the human body. Later the correct temperature of the human body on this scale was found to be 98·4°F. The lower fixed point is marked as 32 and the upper fixed point is marked as 212. The interval is divided into 180 equal parts. Each part or degree represents 1°F.

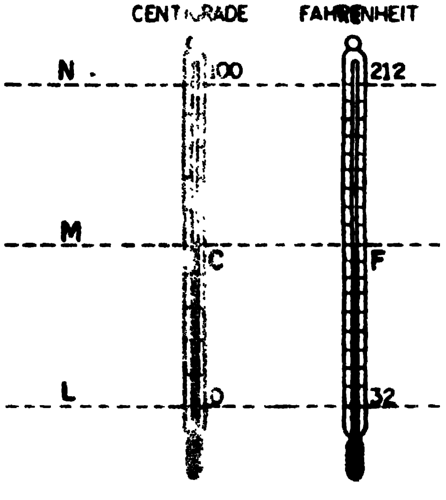


Fig. 1·1

Relation. Consider two identical thermometers marked in Centigrade and Fahrenheit scales. Place the two thermometers in a bath at a certain fixed temperature. Mercury in each thermometer stands to the same level M (Fig. 1·1).

$$\therefore \quad \frac{ML}{NL} = \frac{C-0}{100-0}$$

$$= \frac{F-32}{212-32}$$

or

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

1·5. Relation between Celsius, Kelvin, Fahrenheit and Rankine Scales of Temperature

In Fig. 1·2, the temperatures of the absolute zero, the melting point of ice and the boiling point of water as measured on the Celsius (Centigrade), Kelvin (absolute), Fahrenheit and Rankine scales are shown.

Celsius and Fahrenheit scales show the same reading at −40° *i.e.*, −40°C = −40°F. The Kelvin scale and the Rankine scale agree at zero degree only.

The temperatures represented in Fig. 1·2, have been rounded off to the nearest degree.

Relation.

$$\frac{C-0}{100}=\frac{F-32}{180}=\frac{K-273}{100}=\frac{R-492}{180}$$

Also $$\frac{K}{100}=\frac{R}{180}$$

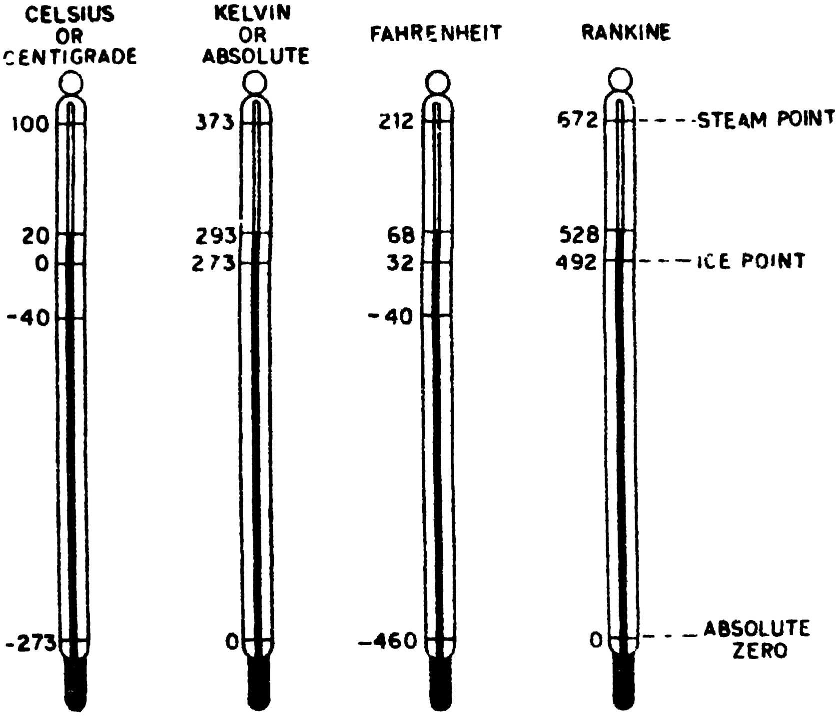


Fig. 1·2

Example 1·1. *The temperature of the surface of the sun is about 6500°C. What is this temperature (i) on the Rankine scale and (ii) on the Kelvin scale ?*

$$\frac{C-0}{100}=\frac{K-273}{100}=\frac{R-492}{180}$$

Here, $C = 6500\ ^\circ\text{C}$

$$\frac{6500}{100}=\frac{K-273}{100}=\frac{R-492}{180}$$

$$K = 6500+273 = 6773\ \text{K}$$

$$R = 12{,}192^\circ\ \text{R}$$

The temperature of the surface of the sun corresponding to 6500°C is (*i*) 6773 K and (*ii*) 12,192° R.

Example 1·2. *The normal boiling point of liquid oxygen is —183°C. What is this temperature on (i) Kelvin scale and (ii) Rankine scale ?*

$$\frac{C-0}{100}=\frac{K-273}{100}=\frac{R-492}{180}$$

Here, $C = -183\ ^\circ\text{C}$

$$\therefore \quad \frac{-183}{100}=\frac{K-273}{100}=\frac{R-492}{180}$$

$$K = 90^\circ\ \text{K}$$

$$R = 162{\cdot}6^\circ\ \text{R}$$

The boiling point of liquid oxygen corresponding to —183°C is (*i*) 90 K and (*ii*) 162·6° R.

Example 1·3. *At what temperature do the Kelvin and Fehrenheit scales coincide ?*

$$\frac{K-273}{100}=\frac{F-32}{180}$$

$$\frac{x-273}{100}=\frac{x-32}{180}$$

$$x = 574{\cdot}25^\circ$$

$$574\text{-}25\ \text{K} = 574{\cdot}25^\circ\text{F}$$

Example 1·4. *At what temperature do the Celsius and the Fahrenheit scales coincide ?*

$$\frac{C-0}{100}=\frac{F-32}{180}.$$

$$\frac{x-0}{100}=\frac{x-32}{180}$$

$$x = -40^\circ$$

$$\therefore \quad -40^\circ\text{C} = 40^\circ\text{F}$$

Example 1·5. *The boiling point of liquid hydrogen is 20·2* K. *Convert this temperature into degree Rankine.*

$$\frac{K-273}{100}=\frac{R-492}{180}$$

Here $K = 20{\cdot}2^\circ\ \text{K}$

$$\therefore \quad \frac{20{\cdot}2-273}{100}=\frac{R-492}{180}$$

$$R = 36{\cdot}96^\circ\ \text{R}$$

$$\therefore \quad 20{\cdot}2\ \text{K} = 36{\cdot}96^\circ\ \text{R}$$

1·6. Liquid Thermometers

Liquid thermometers are based on the principle of change of volume of the liquid with change in temperature. These thermometers are suitable for a narrow range of measurement. The most commonly used liquids are (*i*) mercury and (*ii*) alcohol. The range of mercury thermometer is —39°C to 357°C. Alcohol thermometers are used only to measure temperature near ice point.

Mercury Thermometer

Mercury is usually selected for use in liquid in glass thermometers for the following reasons :

(1) It has a low specific heat and hence it absorbs little heat from the body whose temperature is being measured.

(2) It is a good conductor of heat and takes the temperature of the body quickly.

(3) It can be easily seen in a fine capillary tube and the thermometer can be made sensitive.

(4) It does not wet the wall of the glass tube. This is an important point for the construction of a thermometer.

(5) It has a uniform coefficient of expansion over a wide range of temperature.

(6) It remains a liquid over a large range. Its freezing point is —39°C and the boiling point is 357°C.

1·7 Errors and Corrections in a Mercury Thermometer

(1) **Change of zero.** When a thermometer is graduated after sealing, there will be shift in the zero mark. This is due to the fact that when a thermometer is subjected to a high temperature during construction, glass takes a long time for contraction. Consequently when the thermometer is placed in melting ice, the level of mercury will be above the zero mark (say at +0·5°C). To correct the error, 0·5°C is subtracted from the observed reading. While manufacturing, the sealed thermometer tubes are allowed sufficient time and are graduated after a number of years.

(2) **Recent heating and cooling.** When a thermometer is used to measure a very high temperature, the thermometer bulb expands. If the same thermometer is immediately used to measure low temperature, the level of mercury will be lower than the correct reading. Suppose the thermometer when placed in melting ice, reads —0·3°C, the correction to be applied is +0·3°C.

(3) **Due to exposed stem.** While calibrating a thermometer, the thermometer as a whole is kept in steam. While measuring the temperature, only the bulb is immersed in the bath whose temperature is to be measured. Due to this reason the observed reading is lower than the correct reading. To correct this error, maximum possible length of the stem should be immersed in the bath whose temperature is to be measured.

(4) **Inequality of the bore.** The thermometer is calibrated after marking the lower and the upper fixed points. The distance between the two fixed marks is divided into equal parts assuming that the bore of the thermometer is uniform. If the bore is not uniform, at positions where the bore has lesser diameter, the observed reading is higher than the actual reading. Similarly, when the bore has a higher diameter, the observed reading is less. To correct this error the capillary tube is initially calibrated and a graph is provided which gives the correct readings against the observed readings.

(5) **Position and pressure.** While graduating, if the thermometer was held in the horizontal position and while taking the temperature it is kept in the vertical position, the observed readings will be lower than the correct readings. This is due to the pressure of mercury column. To avoid this error, the thermometer is used in the same position in which it was calibrated.

(6) **Surface tension.** Mercury is depressed in a capillary tube because it does not wet the glass tube. The depression is different at different positions of the stem if the bore is not uniform. To correct this error, the reading of the thermometer is taken with a rising mercury column.

(7) **Thermal capacity.** If the thermal capacity of the bulb is large, a part of the heat from the bath is used in heating the bulb. Therefore, the thermometer reads a lower temperature. To correct this error, small thermometer bulbs with low thermal capacity are used.

(8) **Effect of the bulb.** In a mercury thermometer the glass bulb has an insulating effect. Due to this reason the mercury inside the bulb may not attain the temperature of the bath.

1·8 Gas Equation

Consider a perfect gas at a pressure P, temperature T and volume V.

Let the pressure of the gas change from P to P_1 at constant temperature T such that the volume changes from V to v.

Applying Boyle's law,

$$P_1 v = PV$$

or

$$v = \frac{PV}{P_1} \qquad \dots(i)$$

Now, let the temperature of the gas change from T to T_1 at constant pressure.

Initial Pressure $= P$, Volume $= v$, Temperature $= T$

Final Pressure $= P_1$ Volume $= V_1$, Temperature $= T_1$

Applying Charles' law,

$$\therefore \qquad \frac{v}{T} = \frac{V_1}{T_1} \qquad \dots(ii)$$

Substituting the value of *v* in equation (*ii*)

$$\frac{PV}{TP_1} = \frac{V_1}{T_1} \quad \text{or} \quad \frac{PV}{T} = \frac{P_1V_1}{T_1}$$

$$\therefore \quad \frac{PV}{T} = \text{constant} \qquad \ldots(iii)$$

Universal gas constant. When one gram molecule of a gas at N.T.P. is taken, the constant in equation (*iii*) is R and is called '*universal gas constant*'. Its value is the same for all gases.

$$\frac{PV}{T} = R \quad \text{or} \quad PV = RT \qquad \ldots(i)$$

One gram molecule of a gas at N.T.P. has a volume = 22,400 cc
At normal pressure

$$P = 76 \times 13{\cdot}6 \times 980 \text{ dynes/sq cm}$$

$$V = 22{,}400 \text{ cc}$$

$$T = 273 \text{ K}$$

$$R = \frac{76 \times 13{\cdot}6 \times 980 \times 22{,}400}{273}$$

$$= 8{\cdot}31 \times 10^7 \text{ ergs/g-mol-K}$$

$$R = \frac{8{\cdot}31 \times 10^7}{4{\cdot}2 \times 10^7} = 1{\cdot}986 \text{ cal/g-mol-K}$$

For n gram molecules of a gas, the gas equation is

$$PV = nRT \qquad \ldots(ii)$$

Ordinary gas constant. When one gram of a gas at N.T.P. is taken, the gas constant is r and is known as ordinary gas constant. Its value is different for different gases.

Here $$\frac{PV}{T} = r \quad \text{or} \quad PV = rT$$

(*i*) *For Oxygen.* One gram of oxygen at N.T.P. has a volume

$$= \frac{22{,}400}{32} \text{ cc}$$

$$r = \frac{PV}{T} = \frac{76 \times 13{\cdot}6 \times 980 \times 22{.}400}{273 \times 32}$$

$$= \left(\frac{8{\cdot}31}{32}\right) \times 10^7/\text{ergs/g-K}$$

(*ii*) *For Hydrogen.* One gram of hydrogen at N.T.P. has a volume

$$= \frac{22{,}400}{2} \text{ cc}$$

$$r = \frac{PV}{T} = \frac{76 \times 13{\cdot}6 \times 980 \times 22{,}400}{273 \times 2}$$

$$= \left(\frac{8{\cdot}31}{2}\right) \times 10^7 \text{ ergs/g-K}$$

Similarly r for nitrogen

$$= \left(\frac{8{\cdot}31}{28}\right) \times 10^7 \text{ ergs/g-K}$$

and r for CO_2 $= \left(\frac{8{\cdot}31}{44}\right) \times 10^7$ ergs/g-K

In general,

$$r = \frac{R}{\text{Molecular wt. of the gas in grams}}$$

1·9 Advantages of a Gas Thermometer

1. The coefficient of expansion of gases is very large as compared to liquids. Therefore, gas thermometers are sensitive.

2. The coefficient and the rate of expansion of all gases are the same under similar conditions.

3. The coefficient of expansion of the material of the bulb of the thermometer is negligible in comparison to the coefficient of expansion of a gas.

4. The gases expand uniformly and regularly over a wide range of temperature.

5. The thermal capacity of a gas is low as compared to liquids. Hence even small changes of temperature can be recorded accurately.

6. Gases can be obtained in a pure form.

7. Gas thermometers can be used over a wide range of temperature. They are suitable to measure high and low temperatures.

8. The temperatures measured with a gas thermometer agree with the temperatures on the thermodynamic scale.

Gas thermometers are not suitable for routine work. They are large and cumbersome. They can be used only in one position. They are mainly used to standardize and calibrate other thermometers.

1·10 Callendar's Compensated Constant Pressure Air Thermometer

It is based on the principle that, pressure remaining constant, the volume of a given mass of gas varies directly as its absolute temperature. It consists of a silica bulb A connected to the reservoir R containing mercury (Fig. 1·3). EF is the connecting tube. The compensating bulb B is exactly similar to the silica bulb A. C_1C_2 is the compensating tube having a volume equal to the tube EF.

Initially, the reservoir R is filled with mercury up to the zero mark and the stop-cock is closed. The bulbs A, B and R are immers-

ed in melting ice. The tubes are sealed when the pressure on the two sides as shown by the manometer is the same. *Therefore, pressure of air in A and B is the same.*

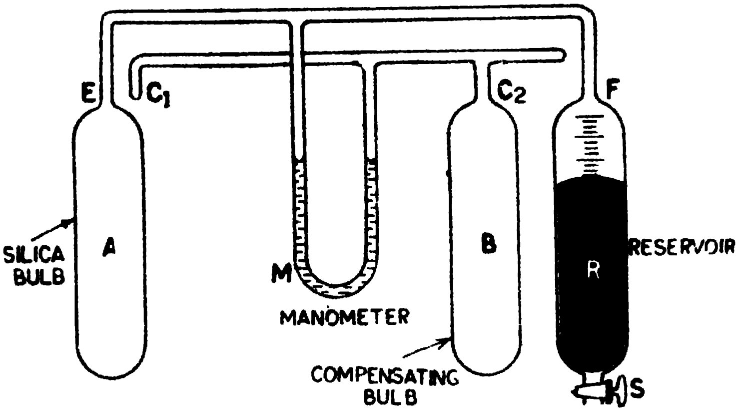


Fig. 1·3

The manometer M contains sulphuric acid. When the pressure on the two sides of the manometer is the same, the levels of sulphuric acid in the two limbs will be the same. In this way the pressure of the gas or air can be maintained constant at all temperatures.

Suppose, the bulb A and the connecting tube EF contain n gram molecules of air. Also the bulb B and the compensating tube C_1C_2 contain n gram molecules of air. The bulb A is immersed in the bath whose temperature is to be measured. The bulb B is kept in melting ice. Tubes EF and C_1C_2 are at the room temperature. The air in the bulb A attains the temperature of the bath. Pressure of air in A increases and the manometer shows the difference in level. Mercury is allowed to flow out of the reservoir R through the stop-cock S and the stop-cock is closed just at the moment when the pressure on the two sides of the manometer is the same.

Volume of the bulb A = Volume of the bulb B = V

Volume of the connecting tube EF = Volume of the compensating tube C_1C_2 = x

Volume of air in the reservoir R at the end = v

Pressure of air on each side = P

Temperature of the bath = T

Room temperature = T_1

Temperature of melting ice = T_0

For the thermometric part,

$$\frac{PV}{T}+\frac{Px}{T_1}+\frac{Pv}{T_0} = nR \qquad \ldots(i)$$

For the compensating part

$$\frac{PV}{T_0}+\frac{Px}{T_1}= nR \qquad \ldots(ii)$$

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

$$\frac{PV}{T}+\frac{Px}{T_1}+\frac{Pv}{T_0}=\frac{PV}{T_0}+\frac{Px}{T_1}$$

$$\frac{V}{T}=\frac{V-v}{T_0}$$

$$T = \left[\frac{V}{V-v}\right]T_0 =\left[\frac{V}{V-v}\right]273 \qquad \ldots(iii)$$

Here T will be obtained in degrees Kelvin

Let the temperature of the bath be t °C

Then, $T = (273+t)$

$$\therefore \quad 273+ t=\left(\frac{V}{V-v}\right)273$$

$$t = \left[\left(\frac{v}{V-v}\right)273\right] °\mathrm{C} \qquad \ldots(iv)$$

This thermometer is useful to measure temperatures upto 600 °C. However, the results obtained with this thermometer are not very accurate.

Example 1·6. *The bulb of the Callendar's compensated constant pressure air thermometer is 1,000* cm³. *When the bulb is immersed in a bath, 100* cm³ *of mercury has to be drawn out of the reservoir. Calculate the temperature of the bath on the Celsius scale.*

Here $V= 1{,}000 \text{ cm}^3$

$v= 100 \text{ cm}^3$

$$t = \left(\frac{v}{V-v}\right)273$$

$$= \left(\frac{100}{1000-100}\right)273$$

$$=30\ 33\ °\mathrm{C}$$

1·11 Jolly's Constant Volume Air Thermometer

It consists of a glass bulb *B* connected to a glass tubing. The end of the glass tube is connected to the reservoir of mercury through a rubber tubing. *M* is a fixed mark on the glass tube. The difference in the levels of mercury in *R* and *M* is observed on the scale *S*. The bulb *B* is filled with 1/7 of its volume with mercury so that the expansion of the bulb *B* is compensated by the expansion of mercury in the bulb. This keeps the volume of air in the bulb up to the mark *M* constant (Fig. 1·4).

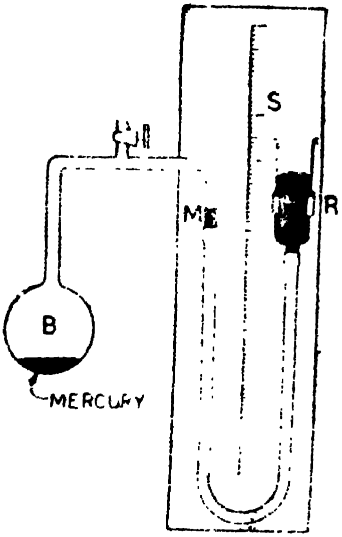


Fig. 1·4

Working. (1) The bulb *B* is kept in melting ice. The reservoir *R* is suitably adjusted so that the level of mercury stands at *M*. Suppose the difference in level between *R* and *M* is h_0. If *P* is the atmospheric pressure, then

$$P_0 = P + h_0. \qquad (i)$$

(2) The bulb *B* is kept in boiling water. The reservoir *R* is adjusted so that the level of mercury is at *M*. Let h_{100} be the difference in levels.

$$P_{100} = P + h_{100} \qquad ...(ii)$$

(3) The bulb *B* is kept in the bath whose temperature is to be measured. The reservoir *R* is adjusted so that the level of mercury is at *M*. Let h_t be the difference in levels.

$$\therefore \quad P_t = P + h_t \qquad ...(iii)$$

Volume remaining constant, the pressure increases according to the relation

$$P_t = P_0\,(1+\gamma t)$$

Also $$P_{100} = P_0\,(1+\gamma 100)$$

or $$P_t - P_0 = P_0 \gamma t \qquad ...(iv)$$

and $$P_{100} - P_0 = P_0 \gamma\, 100 \qquad ...(v)$$

Dividing (*iv*) by (*v*)

$$t = \left(\frac{P_t - P_0}{P_{100} - P_0}\right) \times 100 \qquad ...(vi)$$

$$t = \left(\frac{h_t - h_0}{h_{100} - h_0}\right) \times 100 \qquad ...(vii)$$

Hence *t* can be calculated.

1·12 Constant Volume Hydrogen Thermometer

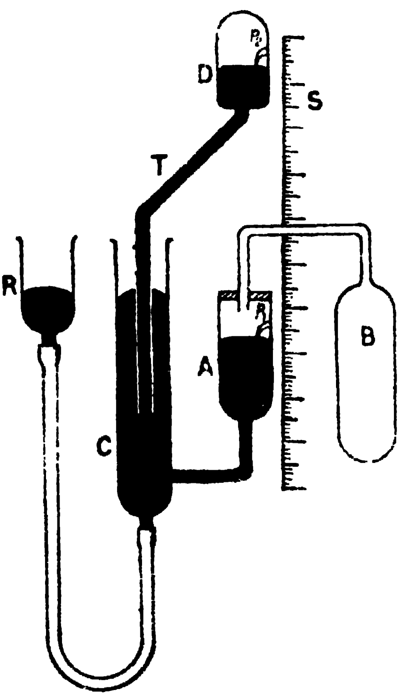


Fig. 1·5

It was first designed by Harker and Chappius and is known as the International standard thermometer. It is based on the principle that when the volume is kept constant, the pressure of a gas increases with rise in temperature according to the relation

$$P_t = P_0\,(1+\gamma t)$$

It consists of a platinum-iridium bulb B connected to the tube A. The reservoir K containing mercury is connected to the tubes C and A as shown in Fig. 1·5. A movable barometric tube T with a bulb D is clamped to a stand. It can be moved vertically up or down as desired. P_1 and P_2 are the two ivory tips in the same vertical line. Above the level of mercury in D, there is Toricellian vacuum (Fig. 1·5).

Working. Initially the bulb is filled with pure dry hydrogen at a pressure higher than the atmospheric pressure.

(1) The bulb B is kept in melting ice. The reservoir R is adjusted so that the level of mercury in A just touches the tip of the ivory peg P_1. The tube T is adjusted so that the level of mercury in D just touches the tip of the ivory peg P_2. Suppose the difference in levels of mercury in A and C is h_0 and the atmospheric pressure is P.

Then $P_0 = P + h_0$. The difference in levels of mercury in C and D is equal to the atmospheric pressure P. It means the distance between the tips of P_1 and P_2 as measured on the scale (or with the help of a cathetometer) gives P_0 directly.

(2) The bulb B is kept in steam or boiling water. R and T are adjusted so that the level of mercury in A just touches the tip of P_1 and that in D just touches the tip of P_2. The difference in the levels of P_1 and P_2 gives P_{100}.

(3) Place the bulb B in the bath whose temperature is to be measured. R and T are adjusted in the same way and the difference in levels of P_1 and P_2 gives P_t.

Here $$P_t = P_0\,(1+\gamma t)$$

$$P_{100} = P_0\,(1+\gamma\, 100)$$

$$\therefore \quad P_t - P_0 = P_0 \gamma t \qquad \ldots(i)$$

$$P_{100} - P_0 = P_0 \gamma\, 100 \qquad \ldots(ii)$$

Dividing (*i*) by (*ii*),

$$t=\left(\frac{P_t-P_0}{P_{100}-P_0}\right)\times 100 \qquad \ldots(iii)$$

The constant volume hydrogen thermometer can be used over a wide range of temperature. With hydrogen and platinum-iridium bulb, the range is —200 °C to 500 °C.

Beyond 500 °C, hydrogen diffuses through platinum. With a porcelain bulb temperatures up to 110 °C can be measured. Beyond 1100°C hydrogen creeps along the wall of the bulb. So it is replaced by nitrogen for measuring temperatures up to 1500 °C. Below —200 °C hydrogen is replaced by helium.

1·13 Gas Thermometer Corrections

While discussing the constant volume hydrogen thermometer, the following assumptions were made :—

(*i*) The whole gas attains the temperature to be measured and that the volume of the gas remains constant.

(*ii*) The gas obeys the perfect gas laws.

'In practice, however, these two assumptions are not true and corrections are to be applied.

First correction. The main sources of error in a constant volume gas thermometer are :

(*i*) The gas in the dead space is not at the same temperature as the gas in the bulb. The dead space consists of the space inside the capillary and in the manometer between the mercury level and the index.

(*ii*) There is increase in the volume of the bulb due to rise in temperature.

(*iii*) There is a change in the volume of the bulb due to change in pressure.

Let the volume of the bulb at 0 °C be V_0 and P_0 the pressure of the gas at 0 °C. Suppose the volume of the dead space is v and the temperature of the dead space throughout the experiment is θ°C. The reduced volume of the whole gas at N.T.P.

$$=\left(V_0+\frac{v}{1+\gamma\theta}\right)\frac{P_0}{76} \qquad \ldots(i)$$

Here γ is the coefficient of expansion of the gas.

When the bulb is heated to t °C, the pressure of the gas becomes (P_0+h).

The reduced volume of the gas at N.T.P. will be,

$$\left\{\left(\frac{V_0(1+\gamma_g t)+bh}{1+\gamma t}\right)+\frac{v}{1+\gamma\theta}\right\}\left(\frac{P_0+h}{76}\right) \qquad \ldots(ii)$$

Here, γ_g is the volume coefficient of expansion of the bulb and b is the volume coefficient of expansion of the bulb due to interna pressure.

Equations (*i*) and (*ii*) represent the reduced volume of the g at NTP at 0 °C and *t* °C. As the mass of the enclosed gas is co ant, these two volumes must be equal.

Equating (*i*) and (*ii*) we get,

$$V_0P_0 = \frac{\{V_0(1+\gamma_g t)+bh\}(P_0+h)}{1+\gamma t}+\frac{vh}{1+\gamma\theta} \qquad \ldots$$

or
$$\gamma t = \left(\frac{P_0+h}{P_0}\right)\left(\frac{V_0(1+\gamma_g t)+bh}{V_0}\right)+\frac{hv}{P_0V_0}\left(\frac{1+\gamma t}{1+\gamma\theta}\right)-1 \qquad \ldots(iv)$$

Here *t* is the temperature of the gas and it occurs on both sides of the equation (*iv*). In case the above corrections are not taken into account, equation (*iv*) reduces to,

$$\gamma t = \frac{h}{P_0}$$

or
$$t = \frac{h}{\gamma P_0} \qquad \ldots(v)$$

Initially the value of *t* is calculated from equation (*v*) and this approximate value is substituted on the right hand side of equation (*iv*). After substituting, a new value of *t* is obtained for the left hand side. This new value is again subsituted on the right hand side and the value of *t* on the left hand side is once again calculated. This method of successive substitution is performed two or three times depending upon the accuracy desired.

1·14. Second Correction (Perfect or Ideal Gas Scale)

All practical gases *viz.* hydrogen, oxygen, nitrogen etc., show deviations from Boyle's law at high pressures and low temperatures. Hence the temperatures obtained with a constant volume or a constant pressure gas thermometer have to be corrected so as to compensate for the departure from the ideal gas. On the constant volume scale, the temperature t_v, is written as,

$$t_v = \left[\frac{P_t-P_0}{P_{100}-P_0}\right]\times 100 \qquad \ldots(i)$$

Similarly on the constant pressure scale the temperature t_p is written as

$$t_p = \left(\frac{V_t-V_0}{V_{100}-V_0}\right)\times 100 \qquad \ldots(ii)$$

If the mass of the gas enclosed is the same in both the thermometers, then at 0 °C, both will have the same pressure P_0 and volume V_0. In the case of constant volume gas thermometer, when the temperature is increased to *t* °C, the pressure becomes P_t. In the constant pressure gas thermometer, at *t* °C, the volume is V_t. If the gas is ideal, in that case

$$V_0P_t = (PV)_t = V_tP_0 \qquad \ldots(iii)$$

Multiplying and dividing the right hand side of equation *(i)*,

$$t_v = \left[\frac{(P_t-P_0)V_0}{(P_{100}-P_0)V_0}\right]\times 100$$

$$t_v \quad \left[\frac{P_tV_0-P_0V_0}{P_{100}V_0-P_0V_0}\right]\times 100 \qquad \ldots(iv)$$

But from equation *(iii)*,

$$P_tV_0 = (PV)_t$$

and

$$P_0V_0 = (PV)_0$$

$$P_{100}V_0 = (PV)_{100}$$

$$\therefore \quad t_v = \left[\frac{(PV)_t-(PV)_0}{(PV)_{100}-(PV)_0}\right]\times 100 \qquad \ldots(v)$$

Similarly it can be shown that

$$t_p = \left[\frac{(PV)_t-(PV)_0}{(PV)_{100}-(PV)_0}\right]\times 100 \qquad \ldots(vi)$$

Thus for an ideal gas, the temperatures measured on the constant pressure scale and constant volume scale are identical and both can be written as

$$t = \left[\frac{(PV)_t-(PV)_0}{(PV)_{100}-(PV)_0}\right]\times 100 \qquad \ldots(v)$$

But in actual practice no gas is ideal.

In the case of real gases, an empirical relation suggested by K-Onnes is

$$PV = A+BP+CP^2+DP^3+\ldots\ldots \qquad \ldots(vi)$$

Here A B, C, D etc., are constants.

These constants are functions of temperature but are independent of pressure. The values of these coefficients are determined by performing compression experiments. These values for oxygen at 0 °C are

$$A = 1{\cdot}00130$$

$$B = -1{\cdot}30143\times 10^{-3}$$

$$C = 3{\cdot}6898\times 10^{-6}$$

Here P is measured in metres of *Hg* and when $P = 1$, V is also equal to one.

It can be seen that the constants A, B, C, D are of rapidly decreasing magnitude In actual practice, for the measurement of temperature, constants C and D are usually neglected. Therefore,

$$PV = A+BP \qquad \ldots(vii)$$

Using equation *(vii)*, it is clear that when $P \to 0$, $PV = A$ or the gas is ideal and obeys Boyle's law.

In order to obtain the temperatures corresponding to an ideal gas, observations are made with a real gas and the values of the temperature, t_{lim} when $P \rightarrow 0$ are obtained. Here t_{lim} will correspond to the ideal gas temperature.

Constant Volume Scale

On the constant volume scale

$$t_v = \left(\frac{P_t - P_0}{P_{100} - P_0} \right) \times 100 \qquad \ldots(viii)$$

From the equation

$$PV = A + BP, \text{ we have}$$

$$\left. \begin{aligned} P_0 V_0 &= A_0 + B_0 P_0 \\ P_{100} V_0 &= A_{100} + B_{100} P_{100} \\ P_t V_0 &= A_t + B_t P_t \end{aligned} \right\} \qquad \ldots(ix)$$

Multiplying and dividing the right hand side of equation (*viii*) by V_0,

$$t_v = \left(\frac{P_t V_0 - P_0 V_0}{P_{100} V_0 - P_0 V_0} \right) \times 100$$

$$\therefore \quad t_v = \left[\frac{(A_t + B_t P_t) - (A_0 + B_0 P_0)}{(A_{100} + B_{100} P_{100}) - (A_0 + B_0 P_0)} \right] \times 100$$

$$t_v = \left[\frac{(A_t - A_0) + (B_t P_t - B_0 P_0)}{(A_{100} - A_0) + (B_{100} P_{100} - B_0 P_0} \right] \times 100$$

$$t_v = \left(\frac{A_t - A_0}{A_{100} - A_0} \right) \times 100 \left[\frac{\left(1 + \dfrac{B_t P_t - B_0 P_0}{A_t - A_0} \right)}{\left(1 + \dfrac{B_{100} P_{100} - B_0 P_0}{A_{100} - A_0} \right)} \right]$$

$$t_v = \left(\frac{A_t - A_0}{A_{100} - A_0} \right) \times 100 \left(1 + \frac{B_t P_t - B_0 P_0}{A_t - A_0} \right) \times \left(1 - \frac{B_{100} P_{100} - B_0 P_0}{A_{100} - A_0} \right)$$

$$t_v = \left(\frac{A_t - A_0}{A_{100} - A_0} \right) \times 100 \left(1 + \frac{B_t P_t - B_0 P_0}{A_t - A_0} - \frac{B_{100} P_{100} - B_0 P_0}{A_{100} - A_0} \right) \qquad \ldots(x)$$

When $P \rightarrow 0$

$$t_{lim} = \left(\frac{A_t - A_0}{A_{100} - A_0} \right) \times 100$$

$$\therefore \quad t_v = t_{lim} \left(1 + \frac{B_t P_t - B_0 P_0}{A_t - A_0} - \frac{B_{100} P_{100} - B_0 P_0}{A_{100} - A_0} \right) \qquad \ldots(xi)$$

$$\text{or} \quad t_{lim} - t_v = t_{lim} \left(\frac{B_{100} P_{100} - B_0 P_0}{A_{100} - A_0} - \frac{B_t P_t - B_0 P_0}{A_t - A_0} \right) \qquad \ldots(xii)$$

Equation (*xii*) gives the correction that has to be applied. The value of t_v is obtained with a thermometer and the value of the constants A_0, B_0, A_t, B_t, A_{100}, B_{100} are obtained by actual compression experiments.

Initially the value of t_v is substituted for t_{lim} on the right hand side of equation (*xii*) and the correction $t_{lim}-t_v$ is calculated. This gives a new value of t_{lim}. This is again substituted on the right hand side and this process of successive substitution is done two or three times. Finally t_{lim} gives the accurate value of temperature on the **ideal gas scale**.

Constant Pressure Scale.

On the constant pressure scale

$$t_p = \left(\frac{V_t-V_0}{V_{100}-V_0}\right) \times 100 \qquad \ldots(xiii)$$

From the equation

$$PV = A+BP \text{ we have}$$

$$P_0V_0 = A_0+B_0P_0$$

$$P_0V_{100} = A_{100}+B_{100}P_0$$

$$P_0V_t = A_t+B_tP_0$$

Multiplying and dividing the right hand side of equation (*xiii*) by P_0,

$$t_p = \left(\frac{P_0V_t-P_0V_0}{P_0V_{100}-P_0V_0}\right)\times 100$$

$$t_p = \left[\frac{(A_t+B_tP_0)-(A_0+B_0P_0)}{(A_{100}+B_{100}P_0)-(A_0+B_0P_0)}\right]\times 100$$

$$t_p = \left(\frac{A_t-A_0}{A_{100}-A_0}\right)\times 100 \left[1+P_0\left(\frac{B_t-B_0}{A_t-A_0}\right) -P_0\left(\frac{B_{100}-B_0}{A_{100}-A_0}\right)\right]$$

When $P \to 0$

$$t_{lim} = \left(\frac{A_t-A_0}{A_{100}-A_0}\right)\times 100$$

$$\therefore \quad t_p = t_{lim}\left[1+P_0\left(\frac{B_t-B_0}{A_t-A_0}\right)-P_0\left(\frac{B_{100}-B_0}{A_{100}-A_0}\right)\right]$$

$$\therefore \quad t_{lim}-t_p = t_{lim}\,P_0\left[\left(\frac{B_{100}-B_0}{A_{100}-A_0}\right)-\left(\frac{B_t-B_0}{A_t-A_0}\right)\right] \qquad \ldots(xiv)$$

Equation (*xiv*) gives the expression for the correction to be applied. The value of t_p is obtained with a thermometer. By the method of successive substitution, the value of t_{lim} is obtained.

From equations (*xii*) and (*xiv*) it is clear that in both the cases the value of

$$t_{lim} = \left(\frac{A_t - A_0}{A_{100} - A_0}\right) \times 100$$

Thus the ideal or perfect gas scale (Celsius scale) can be defined as follows:

$$\underset{\text{(celsius)}}{t} = \left[\frac{\underset{lim\ P \to 0}{(PV)_t} - \underset{lim\ P \to 0}{(PV)_0}}{\underset{lim\ P \to 0}{(PV)_{100}} - \underset{lim\ P \to 0}{(PV)_0}}\right] \times 100 \qquad \ldots (xv)$$

These corrections obtained from equations (*xii*) and (*xiv*) are applicable in the range of – 183°C to 400°C. Beyond 400°C, the corrections are negligibly small.

Example 1.7. *The pressure of air in a constant volume thermometer is 80 cm and 109.3 cm at 0°C and 100 °C respectively. When the bulb is placed in hot water, the pressure is 100 cm. Find the temperature of the hot water.*

(Punjab 1966; Delhi 1973)

$$P_t = 100 \text{ cm of Hg}$$

$$P_{100} = 109.3 \text{ cm of Hg}$$

$$P_0 = 80 \text{ cm of Hg}$$

$$t = \left(\frac{P_t - P_0}{P_{100} - P_0}\right) \times 100 = \left(\frac{100 - 80}{109.3 - 80}\right) \times 100$$

$$t = \mathbf{68.25}\ °\mathrm{C}$$

Example 1.8. *A constant volume hydrogen thermometer is used to measure the temperature of a furnace. The excess pressure in the bulb over the atmospheric pressure is found to be equal to 152 cm of Hg. At 0°C the pressure in the bulb is equal to that of the atmosphere. Calculate the temperature of the furnace, assuming that the atmospheric pressure throughout the experiment remains constant.*

Here

$$P_0 = 76 \text{ cm of Hg}$$

$$P_t = 152 + 76 = 228 \text{ cm of Hg}$$

$$T_0 = 273 \text{ K}$$

$$T = ?$$

$$\frac{P_t}{T} = \frac{P_0}{T_0}$$

$$T = \frac{P_t}{P_0} \times T_0$$

$$T = \frac{228 \times 273}{76}$$

$$T = \mathbf{819\ K} = \mathbf{546}\ °\mathrm{C}$$

1·15 Platinum Resistance Thermometer

It is based on the principle of change of resistance with change in temperature. It was first designed by Siemen in 1871 and later on improved by Callendar and Griffiths.

A platinum resistance thermometer consists of a pure platinum wire wound in a double spiral to avoid inductive effects. The wire is wound on a mica plate. The two ends of the platinum wire are connected to thick copper leads (for lower temperatures) and connected to the binding terminals B_1 B_2. For higher temperatures the leads are of platinum. C_1 and C_2 are the compensating leads exactly similar and of the same resistance as the leads used with the platinum wire. The platinum wire and the compensating leads are enclosed in a glazed porcelain tube. The tube is sealed and binding terminals are provided at the top. The leads pass through mica discs which offer the best insulation and also prevent convection currents (Fig. 1·6).

The resistance of a wire at t°C $= R_t$ and at 0°C $= R_0$. These resistances are connected by the relation

$$R_t = R_0\,(1+\alpha t+\beta t^2). \qquad \ldots(i)$$

Here α and β are constants. The values of α and β depend on the nature of the material used. To find the values of α and β, the resistance of the platinum wire is determined at three fixed points (*i*) melting point of ice, (*ii*) boiling point of water, (*iii*) boiling point of sulphur 444·6°C for high temperature measurement and (*iv*) boiling point of oxygen —182·5°C for low temperature measurement.

Using these values of resistance in equation (*i*)

$$R_{100} = R_0[1+\alpha\;100+\beta 100^2] \qquad \ldots(ii)$$

and

$$R_{444\cdot 6} = R_0[1+\alpha\;444\cdot 6+\beta(444\cdot 6)^2] \qquad \ldots(iii)$$

The values of α and β can be determined by solving the simultaneous equations (*ii*) and (*iii*).

From (*i*) $\quad R_t = R_0[1+\alpha t+\beta t^2]$

Neglecting βt^2 (because β is very small)

$$R_t = R_0\,[1+\alpha t] \qquad \ldots(iv)$$

and

$$R_{100} = R_0[1+\alpha\times 100]$$

$$\therefore \quad R_t-R_0 = R_0\,\alpha\,t \qquad \ldots(v)$$

$$R_{100}-R_0 = R_0\,\alpha.\,100 \qquad \ldots(vi)$$

Dividing (*v*) and (*vi*)

$$\frac{R_t-R_0}{R_{100}-R_0} = \frac{t}{100}$$

$$t = \left(\frac{R_t-R_0}{R_{100}-R_0}\right)\times 100 \qquad \ldots(vii)$$

Knowing the values of R_0, R_{100} and R_t, t can be calculated.

The resistance of the platinum wire is found accurately using Callendar and Griffiths' bridge.

Callendar and Griffith's Bridge

This is a modified form of Wheatstone's bridge, used to measure the change in resistance with temperature of the platinum wire used in a platinum resistance thermometer.

P and Q are two resistances of equal value and S is a standard fractional resistance box. The platinum wire whose resistance is to be calculated is connected in one of the arms of the Wheatstone's bridge as shown in Fig. 1·6. The compensating leads are connected in series with the resistance S. XY is the bridge wire of length $2l$ and of resistance per unit length ρ. Let r be the resistance of the compensating leads and O the mid-point of the bridge wire. R is the resistance of the platinum wire at the temperature of the bath. Let D be the balance point, with some suitable value of S, x cm to the left of O.

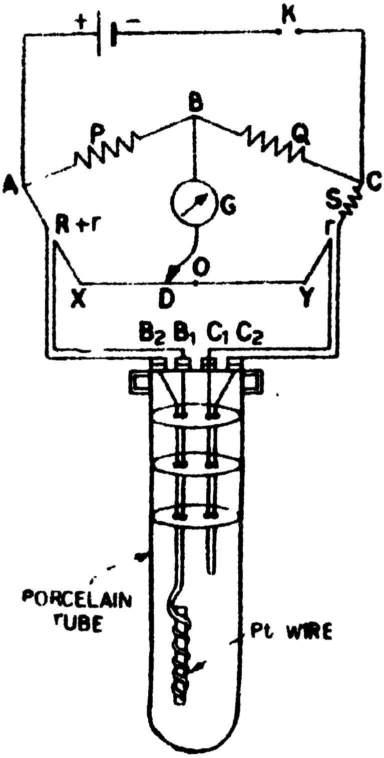


Fig. 1·6

Then length $XD = l-x$

$DY = l+x$

As $P = Q$, the resistance of the arm AD = resistance of the arm CD

$$\therefore \quad R+r+(l-x)\rho = S+r+(l+x)\rho$$

$$R+r+l\rho-x\rho = S+r+l\rho+x\rho$$

$$R = S+2x\rho$$

(If the balance point is obtained to the right of O, it can be shown that $R = S-2x\rho$).

Thus, using a Callendar and Griffith's bridge the resistance R_t of the platinum wire can be determined at temperature t.

A scale can be fixed along the bridge wire XY to read platinum scale temperatures directly. The range will be different for different values of S.

Correction. The temperature t measured on the platinum scale according to equation (*vii*) is not accurate because βt^2 term has been neglected. Therefore, the correct thermodynamic temperature θ will differ from t.

Here $$\theta-t = \delta\left[\left(\frac{\theta}{100}\right)^2-\left(\frac{\theta}{100}\right)\right] \qquad \ldots(viii)$$

The value of δ can be calculated by knowing the values of α and β.

Equation (*viii*) can be derived as follows :

$$\theta-t = \theta-\left(\frac{R_t-R_0}{R_{100}-R_0}\right)\times 100$$

Take $$R_t = R_0(1+\alpha\theta+\beta\theta^2)$$

and $$R_{100} = R_0\,[1+\alpha\,100+\beta(100)^2]$$

$$\therefore \quad \frac{R_t-R_0}{R_{100}-R_0} = \frac{\alpha\theta+\beta\theta^2}{\alpha 100+\beta\;(100)^2}$$

$$\therefore \quad \theta-t = \theta-\left(\frac{\alpha\theta+\beta\theta^2}{\alpha+\beta\;100}\right)$$

$$\theta-t = \frac{\alpha\theta+100\beta\theta-\alpha\theta-\beta\theta^2}{\alpha+\beta\;100}$$

$$\theta-t = \frac{100\beta\theta-\beta\theta^2}{(\alpha+\beta\;100)}$$

$$\theta-t = \frac{-(100)^2\,\beta}{(\alpha+\beta\;100)}\left[\frac{\theta^2}{(100)^2}-\frac{\theta}{100}\right]$$

$$\theta-t = \delta\left[\left(\frac{\theta}{100}\right)^2-\left(\frac{\theta}{100}\right)\right] \qquad \ldots(ix)$$

Here $$\delta = \frac{-(100)^2\,\beta}{(\alpha+\beta\;100)}$$

The value of δ for pure platinum is approximately equal to 1·5.

Advantages. The platinum resistance thermometer can be used with great accuracy to measure temperatures ranging from −200°C to 1200°C. Its accuracy is 0·1°C. Once the platinum resistance thermometer has been standardised with a constant volume hydrogen thermometer, it can be used as a standard thermometer.

Its main disadvantage is that the adjustment of the Callendar and Griffiths' bridge takes a long time. Moreover, the wire may not attain the temperature of the bath in a short time.

Example 1·9. *The resistance of the platinum wire of a platinum resistance thermometer at the ice point is 5* ohms *and at the steam point 5·93* ohms. *The pressure exerted by the gas in a constant volume gas thermometer is (i) 100* cm *of* Hg *at ice point (ii) 136·6* cm *of* Hg *at the steam point. When both the thermometers are inserted in a hot bath the resistance of the platinum wire is 5·795* ohms *and the pressure of the gas is 131·11* cm *of* Hg. *Calculate Celsius temperature of the bath (i) on the platinum scale and (ii) on the gas scaled*

(Berhampur 1972)

(*i*) On the platinum scale

$$R_0 = 5 \text{ ohms}$$

$$R_{100} = 5{\cdot}23 \text{ ohms}$$

$$R_t = 5{\cdot}795 \text{ ohms}$$

$$t_p = \left(\frac{R_t - R_0}{R_{100} - R_0}\right) \times 100$$

$$= \left(\frac{5{\cdot}795 - 5}{5{\cdot}93 - 5}\right) \times 100 = \mathbf{85{\cdot}48^\circ C}$$

(*ii*) On the gas scale

$$P_0 = 100 \text{ cm Hg}$$

$$P_{100} = 136{\cdot}6 \text{ cm Hg}$$

$$P_t = 131{\cdot}11 \text{ cm Hg}$$

$$t = \left(\frac{P_t - P_0}{P_{100} - P_0}\right) \times 100$$

$$= \left(\frac{131{\cdot}11 - 100}{136{\cdot}6 - 100}\right) \times 100 = \mathbf{85^\circ C}$$

Example 1·10. *If the platinum temperature, corresponding to 50°C on the gas scale is 50·25°, what will be the temperature on the platinum scale corresponding to 150°C on the gas scale ?*

Let θ be the temperature on the gas scale and t on the platinum scale.

Let
$$\theta - t = \delta\left[\left(\frac{\theta}{100}\right)^2 - \left(\frac{\theta}{100}\right)\right]$$

$$\theta = 50^\circ \; ; \; t = 50{\cdot}25$$

$$\therefore \quad 50 - 50{\cdot}25 = \delta\left[\left(\frac{50}{100}\right)^2 - \left(\frac{50}{100}\right)\right] \qquad ...(i)$$

(*ii*)
$$\theta = 150^\circ \; ; \; t = x$$

$$\therefore \quad 150 - x = \delta\left[\left(\frac{150}{100}\right)^2 - \left(\frac{150}{100}\right)\right. \qquad ...(ii)$$

Dividing (*ii*) by (*i*) and simplifying

$$x = \mathbf{149{\cdot}25^\circ C}$$

Example 1·11. *The resistance of a platinum wire at 0°C, 100°C and 444·6°C is found to be 5·5, 7·5 and 14·5 ohms respectively. The resistance of a wire at a temperature t°C is given by the equation*

$$R_t = R_0(1+\alpha t+\beta t^2)$$

Find the values of α and β.

Here

$$R_0 = 5{\cdot}5 \text{ ohms}$$

$$R_{100} = 7{\cdot}5 \text{ ohms}$$

$$R_{444{\cdot}6} = 14{\cdot}5 \text{ ohms}$$

$$R_t = R_0(1+\alpha t+\beta t^2)$$

$$\therefore \quad R_{100} = R_0[1+\alpha(100)+\beta(100)^2] \qquad \ldots(i)$$

$$R_{444{\cdot}6} = R_0[(1+\alpha(444{\cdot}6)+\beta(444{\cdot}6)^2] \qquad \ldots(ii)$$

∴ Substituting the values in equations (*i*) and (*ii*)

$$7{\cdot}5 = 5{\cdot}5[1+100\alpha+(100)^2\,\beta] \qquad \ldots(iii)$$

$$14{\cdot}5 = 5{\cdot}5[1+444{\cdot}6\alpha+(444{\cdot}6)^2\,\beta] \qquad \ldots(iv)$$

Simplifying equations (*iii*) and (*iv*)

$$\alpha+100\beta = \frac{2}{5{\cdot}5\times100} \qquad \ldots(v)$$

$$\alpha+444{\cdot}6\,\beta = \frac{9}{5{\cdot}5\times444{\cdot}6} \qquad \ldots(vi)$$

Subtracting equation (*v*) from (*vi*)

$$344{\cdot}6\,\beta = \frac{900-2\times444{\cdot}6}{5{\cdot}5\times444{\cdot}6\times100}$$

$$\therefore \quad \beta = \mathbf{1{\cdot}281\times10^{-7}/^\circ C^2}$$

Substituting the value of β in equation (*v*)

$$\alpha+100(1{\cdot}281\times10^{-7}) = \frac{2}{5{\cdot}50\times100}$$

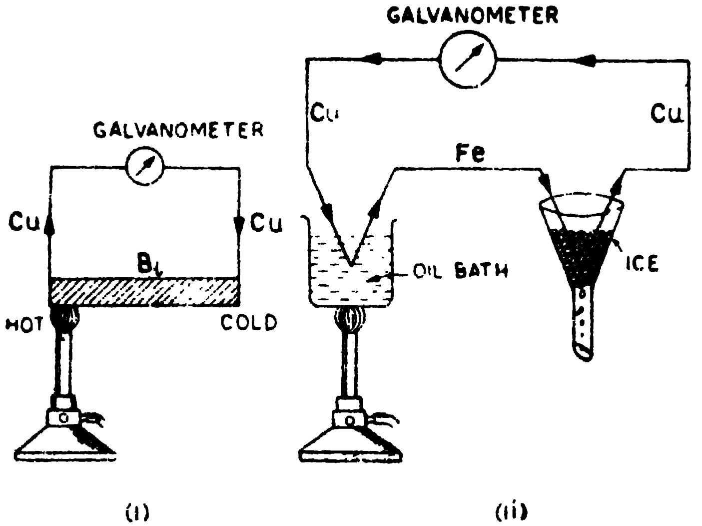
$$\alpha = 363{\cdot}6\times10^{-5}-1{\cdot}281\times10^{-5}$$

$$\alpha = 362{\cdot}319\times10^{-5}$$

$$\alpha = \mathbf{3{\cdot}62\times10^{-3}/^\circ C}$$

1·16 Seebeck Effect

In 1821, Seebeck found that a current flows in a circuit consisting of two dissimilar metals when one junction is heated while the other junction is kept cold. This was a remarkable experiment because ***no cell*** was used in the circuit. He connected a plate of bismuth between copper wires connected to a galvanometer [Fig. 1·7 (*i*)]. He found that if one of the junctions was heated while the other was kept cold, then a current flowed through the galvanometer. He repeated his experiment by taking a thermo-couple of Fe and Cu [Fig. 1·7 (*ii*)].



F'g. 1·7

If both the junctions are at 0°C, there is no deflection in the galvanometer. When one of the junctions is kept at 0°C, *i.e.*, at the temperature of melting point of ice and the other junction is heated gradually, current flows in the circuit. It was found that current flows from copper to iron at the hot junction and iron to copper at the cold junction. The current increases until the hot junction is at a temperature of 270°C. If the heating is continued beyond 270°C, the current decreases and finally at 540°C the current is zero.

It was discovered by ***Cumming*** in 1823 that, on increasing the temperature of the hot junction beyond 540°C, the direction of the current is reversed. It flows from iron to copper through the hot junction and copper to iron through the cold junction.

The current produced in this way without the use of a cell or a battery is known as ***thermo-electric current*** and this branch of electricity is known as thermo-electricity. The effect is known as ***Seebeck effect.***

The temperature of the hot junction at which maximum current flows in a circuit is known as ***neutral temperature*** for that couple. The neutral temperature for a given thermocouple is fixed and remains constant whatever may be the temperature of the cold junction. The E.M.F. produced in this way is called ***thermo-E.M.F.***

If a graph is plotted between the temperature of the hot junction and the thermo-E.M.F., the cold junction being kept at 0°C the graph is a parabolic curve. The thermo-E.M.F. E varies with temperature according to $E = at+bt^2$, where a and b are constants. The point A represents the neutral temperature. The point B is the ***temperature of inversion***, beyond which the current is reversed (Fig. 1·8).

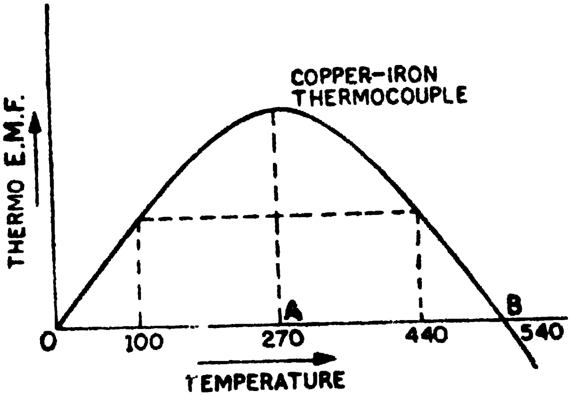


Fig. 1·8

The temperature of inversion is not fixed. It is as much above the neutral temperature as the cold junction is below the neutral temperature.

Suppose the temperature of the cold junction $= \theta_1$

Neutral temperature $= \theta_n$

Temperature of inversion $= \theta_2$

Then, $\theta_n-\theta_1 = \theta_2-\theta_n$, or $\theta_n = \left(\frac{\theta_1+\theta_2}{2}\right)$

In the case of Cu—Fe thermocouple, if the cold junction is at 100°C temperature of inversion = 440°C.

1·17 Thermo-Electric Thermometer

It is based on the principle of Seebeck effect [Refer article 1·16]. Two dissimilar metals are selected. The thermo-E.M.F. produced, depends upon the difference of temperature between the hot and the cold junctions. For measuring temperatures up to 300°C, copper-constantan thermocouple is used. Iron-nickel is used between 300°C and 600°C and nickel-nichrome is used between 600°C and 1000°C. For temperatures between 1000°C and 1600°C, a thermocouple of platinum and an alloy of platinum and rhodium is used. Beyond 1600°C, up to 2000°C iridium and an alloy of iridium and rubidium is used. For measuring temperatures between 2000°C and 3000°C, tungsten and molybdenum thermocouple is used.

The hot junction is made by welding the junction of two metals and the junction is enclosed in a fine capillary tube. The whole arrangement is enclosed in an outer porcelain tube (Fig. 1·9). The wires 1 and 2 inside the tube are kept separate with the help of mica strips.

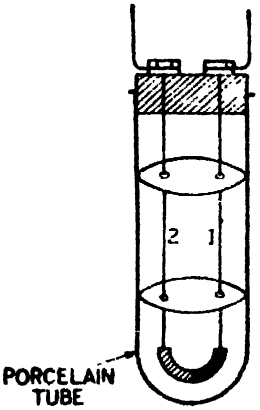


Fig. 1·9

Measurement of Temperature

The most important part of the experiment for the measurement of temperature is the accuracy with which the thermo-E.M.F. can be measured. Two methods are usually employed, *e.g.*

(*i*) Using a sensitive galvanometer,

(*ii*) Using potentiometer.

(1) **Using a galvanometer.** A sensitive galvanometer is connected with the thermo couple (Fig. 1·10). One of the junctions is kept in melting ice (0°C) and the other junction in an oil bath. The oil bath is heated and thermo-E.M.F. is produced in the circuit. The temperature of the oil bath is determined by using a constant volume hydrogen thermometer or some other sensitive thermometer.

Corresponding to the various temperatures of the hot junction (oil bath) the corresponding deflections in the galvanometer are observed. A graph is plotted between the deflection along the y-axis and the temperature of the hot junction along the x-axis (Fig. 1·11). Thus for the given thermocouple the galvanometer is calibrated.

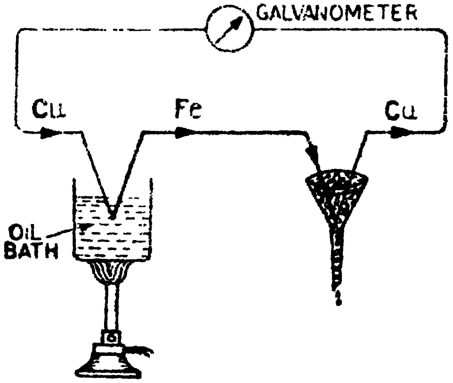


Fig. 1·10

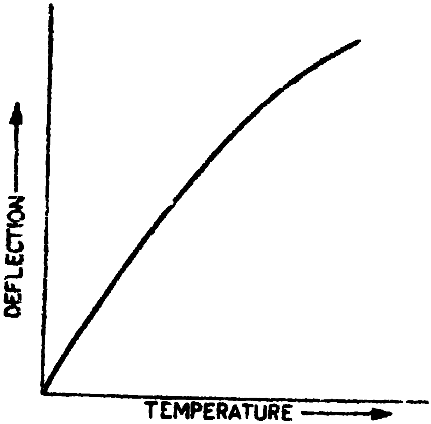


Fig. 1·11

The bath whose temperature is to be measured, is taken. The hot junction of the thermocouple is immersed in the bath, other junction being kept in melting ice. The deflection produced in the galvanometer is observed. From the graph, the corresponding value of temperature is determined. Moreover, the scale of the galvanometer can be directly marked in °C to show the temperatures directly. Such a thermo-electric thermometer is not very sensitive.

(2) **Using a Potentiometer.** The thermo- E.M.F. produced in a thermocouple is of the order of 10^{-5} volt. Therefore the potentiometer should be sensitive to measure up to 10^{-6} volt. For this purpose the circuit used is as shown in Fig. 1·12. To check the correctness of the connections, first close the key α. If on closing the key K, the deflection in the galvanometer decreases, then the connections are correct.

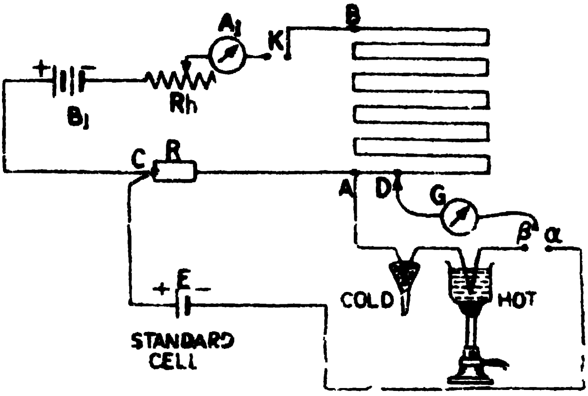


Fig. 1·12

The standard cadmium cell E has an E.M.F. = 1·0183 volts. The potentiometer has ten wires of length one metre each. The potentiometer whose wire has a resistance of one ohm per metre is used. The distance AD = 30 cm. The jockey is kept at D.

A resistance of 1018 ohms is introduced in R and the key α is closed. The rheostat Rh is adjusted so that the deflection in the galvanometer is zero. Then, the P.D. across CD = 1·0183 volts.

The resistance of $AD = \dfrac{1 \times 30}{100} = 0{\cdot}3$ ohm

The resistance of $CD = 1018 + 0{\cdot}3 = 1018{\cdot}3$ ohm

Fall of potential for one ohm-resistance

$$= \frac{1{\cdot}0183}{1018{\cdot}3} = 10^{-3} \text{ volt}$$

The potentiometer wire has a resistance of one ohm per metre. Therefore the fall of potential for one metre length of the potentiometer wire = 10^{-3} volt and the fall of potential per mm length of the potentiometer wire

$$= \frac{10^{-3}}{1000} = 10^{-6} \text{ volt per mm.}$$

Thus the potentiometer wire is calibrated.

The key α is taken out and the key β is introduced. For the various temperatures of the hot junction, the corresponding balance points are observed. The lengths are measured from the point A. Thus the corresponding thermo- E.M.F. produced in the circuit can be calculated. The temperatures of the hot junction are measured with a standard constant volume hydrogen thermometer. A graph is plotted between the thermo-E.M.F. produced and the corresponding temperature. The potentiometer wire can be directly calibrated to measure the temperatures.

The hot junction is kept in the bath of the furnace whose temperature is to be measured and the balance point is found. From the balancing length, the corresponding temperature is either read from the graph or from the chart provided.

For practical purposes charts are provided with each thermo-couple.

Advantages. (1) It has a wide range and can measure temperatures from —200°C up to 3000°C. (2) It is useful to measure rapidly varying temperatures. (3) It can be easily constructed and it is cheap. (4) It is useful to measure the temperature of hot furnaces and does not require any calculations, once it has been calibrated.

Limits and Drawbacks. This thermometer does not give accurate temperatures over a wide range. Different thermocouples are to be used for different ranges. The potentiometer is to be calibrated for different thermo-couples separately. Moreover, the neutral temperature of a thermo-couple also limits its range.

1·18 Helium Vapour Pressure Thermometer

This thermometer is used to measure temperature up to 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· 1·13).

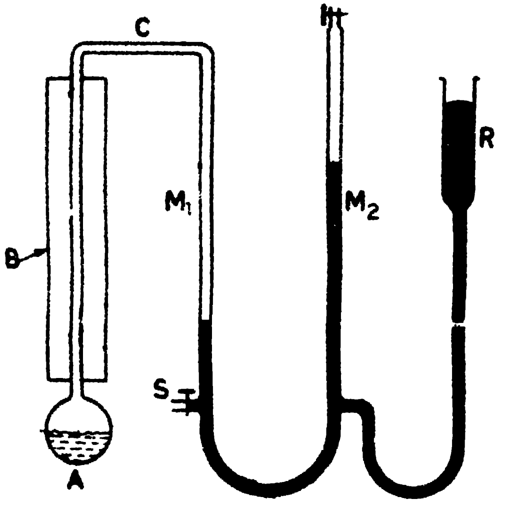


Fig. 1·13

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.

Table

Vapour pressure of helium (He^4) at different temperatures

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	23·2
1·50	3·6
1·00	0·12
0·40	$1\ 6 \times 11^{-5}$
0·10	$3{\cdot}4 \times 10^{-32}$

1·19 Standardization and Temperature Scale

The various thermometers depend upon the property of a substance. The temperature scale shown by a thermometer will also depend on the property of the substance selected. Due to this reason, the scale of temperature is arbitrary depending on the property of the substance. The thermometers thus manufactured agree only at the fixed points and not at any other temperature.

Let the magnitude of the property selected be

x_t, x_{ice}, x_{steam} at t°C, 0°C and 100°C.

The temperature t can be calculated from the relation

$$\frac{t}{100} = \frac{x_t - x_{ice}}{x_{steam} - x_{ice}} \qquad \ldots(i)$$

It means that the temperature scale selected and the property of the substance chosen vary uniformly. But it has been found that the properties of a substance *e.g.* expansion with rise in temperature in mercury thermometer, change of resistance with temperature in a platinum resistance thermometer etc. do not vary uniformly at all temperatures. Due to this reason, all the thermometers do not show the same temperature readings at one fixed temperature. Suppose the temperature of the liquid is measured by (*i*) a mercury thermometer (*ii*) a constant volume hydrogen thermometer and (*iii*) a platinum resistance thermometer at the same time. All these thermometers will not show the same reading. The readings may be 40·11°C, 40°C, and 40·36°C. Thus it is found that the temperature shown by the thermometer depends, upon the nature of the thermometer used. However, these thermometers will show the same temperatures at fixed points *e.g.* melting point of ice and boiling point of water.

Comparison of different thermometers

Constant volume hydrogen thermometer	*Pt. resistance thermometer*	*Mercury thermometer*
0°C	0°C	0°C
20°C	20·24°C	20·09°C
60°C	60·36°C	60·09°C
100°C	100°C	100°C

In 1887, an international committee of scientists suggested that a scale of temperature shown by constant volume hydrogen thermometer be taken as a standard scale, 0°C being that of melting ice and 100°C being the temperature of steam at normal pressure. But hydrogen also is not a standard or a perfect gas.

Later on it was thought that temperature scale suggested by Kelvin be used as a standard scale because it does not depend upon property of a substance. The Kelvin scale of temperature (K) [work scale] agrees with the absolute gas scale.

As it appears difficult to realize the Kelvin scale in practice it is suggested in 1933 that an international scale of temperature be adopted. The melting point of ice and boiling point of pure water at normal pressure etc. are given the fixed values and the temperatures between these points are calculated by a specific formula. The international scale of temperature is the nearest practical approach to the Kelvin scale of temperature

Fixed Points

(1) **Oxygen point.** Temperature of equilibrium between liquid oxygen and gaseous oxygen at normal pressure = —182·97°C.

(2) **Ice point.** Temperature of equilibrium between ice and air saturated water at normal pressure = 0·000°C.

(3) **Steam point.** Temperature of equilibrium between liquid water and its vapour at normal pressure = 100·000°C.

(4) **Sulphur point.** Temperature of equilibrium between liquid sulphur and its vapour at normal pressure = 444·60°C.

(5) **Silver point.** Temperature of equilibrium between solid silver and liquid silver at normal pressure = 960·8°C.

(6) **Gold point.** Temperature of equilibrium between solid gold and liquid gold at normal pressure = 1063°C.

The scale is divided into four parts for the purpose of determining the temperature between two fixed points.

(*a*) **From —190°C to 0°C.** The platinum resistance thermometer is used and the relation is

$$R_t = R_0\,[1+\alpha t+\beta t^2-\gamma\,(t-100)\,t^3]$$

(*b*) **From 0°C to 660°C.** The platinum resistance thermometer is used and the relation is

$$R_t = R_0\,(1+\alpha t+\beta t^2)$$

(*c*) **From 660°C to 1063°C.** The thermocouple of platinum and an alloy of platinum-rhodium is used. One junction is kept in melting ice. The thermo-E.M.F. produced is measured and the relation used is

$$E = \alpha+\beta t+\gamma t^2$$

(*d*) **Beyond 1063°C.** The ratio of the intensities of monochromatic heat radiation emitted by the black body at t°C and at 1063°C is determined and the temperature is calculated using Planck's radiation law.

1·20 Absolute Zero and Ice Point

For approximate purposes, the value of absolute zero or zero degree Kelvin is taken as —273°C. But near about absolute zero its correct determination is a necessity. For accurate work the value of absolute zero is taken as —273·16°C. Similarly the temperature of melting point of ice was suggested by the International Advisory Committee of Thermometry in 1948, as 273·15 K. But in 1954, the international committee fixed 273·16 K (triple point of water) as ice point. Thus for accurate purposes,·

Ice point = 0°C = 273·16 K

Steam point = 100°C = 373·16 K

Zero degree Kelvin = —273·16°C.

1·21 Low Temperature Measurement

The various thermometers used to measure low temperatures are discussed below :

(1) *Liquid Thermometers.* With alcohol thermometer temperatures up to —100°C can be measured. With mercury in glass, temperatures up to —30°C can be measured. The accuracy is about 0·1°C. These are convenient and their response is quick.

(2) *Gas Thermometers.* Constant volume hydrogen thermometer can be used to measure up to —250°C and with constant volume helium thermometer temperatures up to —268°C can be determined. These thermometers are quite accurate but they are quite bulky.

(3) *Resistance Thermometers.* With platinum resistance thermometers temperatures up to —190°C can be measured accurately. Its accuracy is 0·01°C. It is quite accurate but its response is slow.

(4) *Thermo-electric Thermometers.* With copper-constantan thermocouple or platinum and silver thermocouple, temperatures up to —250°C can be measured. Its accuracy is 0·05°C.

(5) *Vapour Pressure Thermometers.* These can be used to measure up to —268°C. Below —268°C, helium vapour pressure thermometer is used. It can be used up to —272°C.

(6) *Magnetic Thermometer.* Near about the absolute zero temperature, magnetic thermometers are used. They are based upon the principle of change in susceptibility with temperature according to Curie's law.

1·22 High Temperature Measurement

The various thermometers used to measure high temperatures are given below :

(1) *Liquid Thermometers.* Mercury in glass can measure up to 300°C. If the space above mercury is filled with some inert gas like nitrogen or helium, it can be used up to 600°C.

(2) *Gas Thermometers.* Constant volume hydrogen thermometer having a platinum bulb, can be used to measure up to 500°C. With a porcelain bulb temperatures up to 1100°C can be measured. Beyond 1100°C, using nitrogen in place of hydrogen, temperatures up to 1500°C can be measured. They are quite bulky for use.

(3) *Resistance Thermometers.* The platinum thermometer can be used up to 1200°C when properly calibrated. Its accuracy is 0·1°C. It is a slow measuring instrument.

(4) *Thermo-electric Thermometers.* For measuring up to 300°C copper-constantan thermocouple is used. Iron-nickel thermocouple is used between 300°C and 600°C. Nickel-nichrome thermocouple is used between 600°C and 1000°C. A thermocouple of platinum and rhodium is used between 1000°C and 1600°C. Between 1600°C and 2000°C a thermocouple of iridium and an alloy of iridium and rubidium is used. For measuring between 2000° and 3000°C, tungsten and molybdenum thermocouple is used.

(5) *Pyrometers.* For measuring the temperature of furnaces and the sun, optical pyrometers are used.

Exercises 1

1. Write an essay on the measurement of high and low temperatures. (*Agra 1960, 1961*)

2. State with reasons the type of thermometer which you

consider most suitable for use at temperatures (*a*) −250°C (*b*) 700°C and (*c*) 2000°C. Indicate briefly the methods of their use. (*Agra 1962*)

3. Describe a platinum resistance thermometer. Explain how it works with the help of Callendar and Griffith's bridge. How does the platinum temperature of a body differ from its true temperature ? (*Agra 1963, 1966*; *Delhi 1960*; *Lucknow 1963*; *Berhampur 1972*)

4. What do you understand by the absolute scale of temperature ? Is the negative temperature possible on this scale ? (*Agra 1964*)

5. Describe the Callendar and Griffith's method of determining the temperature coefficient of platinum. In what respects it is superior to Carey Foster's method ? What do you understand by (*i*) platinum leads (*ii*) compensating arm (*iii*) non-inductive winding of the platinum wire ? (*Agra 1965*)

6. Give the theory and construction of a constant volume gas thermometer. In what respects is this thermometer superior to mercury in glass thermometer ? (*Punjab 1962*)

7. Give an account of the thermoelectric thermometry and discuss the range, sensitivity and usefulness of some important thermocouples. (*Lucknow 1964*)

8. Describe carefully the methods for measuring low temperatures in the range −100°C to −273°C. Explain the concept of absolute zero of temperature. (*Rajasthan 1964*)

9. State the advantages of using a permanent gas as a thermometric substance. Describe the working of a constant volume hydrogen thermometer. (*Madras 19[illegible]4, Delhi 1968*)

10. Describe a resistance thermometer. Explain how it is used to measure temperatures accurately. Discuss its advantages over a thermo-electric thermometer. (*Delhi 1969*)

11. Describe and explain how the platinum resistance thermometer can be used to measure temperatures accurately in the region 200°C to 500°C. (*Delhi 1971, 76*)

12. Give the construction of a thermoelectric thermometer and compare its performance with a standard gas thermometer. What precautions should be taken in measuring temperatures with a thermoelectric thermometer ? (*Delhi 1972, 76*)

13. Describe the construction and working of a standard gas thermometer. (*Delhi 1973, 76*)

14. What is meant by a scale of temperature ? On what does the definition of any particular scale depend ? (*Delhi 1975*)

15. Give a detailed account of the experiment you would perform to determine the temperature of boiling aniline on the platinum resistance scale of temperature. By how much does the temperature measured by this thermometer differ from that measured by gas thermometer ? (*Delhi 1975*)

16. Discuss the advantages of using one of the permanent gases as a thermometric substance for defining a scale of temperature. Describe some convenient and accurate form of gas thermometer. Explain its mode of use and show how the temperature is calculated from the observations made with it. *(Delhi 1975)*

17. State briefly the principles underlying the working of the following thermometers :

(*i*) Constant volume gas thermometer.
(*ii*) Resistance thermometer.
(*iii*) Thermo-electric thermometer
(*iv*) Vapour-pressure thermometer. *(Delhi 1974)*

18. Describe Callendar and Griffith's bridge for measuring the resistance of a platinum resistance thermometer at various temperatures. Deduce by how much a temperature measured by this thermometer differs from that measured by a gas thermometer. *(Delhi 1974)*

19. Describe a platinum resistance thermometer. How would you calibrate and use it for measuring the temperature of a body ? Mention the advantages of this thermometer. *(Delhi 1976)*

20. On what principle is the working of a platinum resistance thermometer based ? Describe Callendar and Griffiths bridge for the accurate measurement of resistance. How is the true temperature deduced from the measured platinum temperature ? *[Delhi, 1978]*

21. Write short notes on :—

(*i*) Callendar's compensated constant pressure air thermometer
(*ii*) Platinum resistance thermometer.
(*iii*) Constant volume hydrogen thermometer.
(*iv*) Thermo-electric thermometer.
(*v*) Measurement of high temperature.
(*vi*) Measurement of low temperature.
(*vii*) Rankine and Kelvin scales of temperature.
(*viii*) Errors and corrections in mercury thermometers.
(*ix*) Advantages of gas thermometers.
(*x*) Universal gas constant.

22 The temperature of a furnace is 2000°C. What is this temperature (*i*), on the Rankine scale and (*ii*) on the Kelvin scale ? [**Ans.** (*i*) 4092°R ; (*ii*) 2273 K]

23 The normal boiling point of liquid hydrogen is −253°C. What is this temperature (*i*) on the Kelvin scale and (*ii*) on the Rankine scale ? [**Ans.** (*i*) 20 K ; (*ii*) 36·6°R]

24. At what temperature will the Kelvin scale reading be double the Fahrenheit reading ? [**Ans.** 176·7°F = 353·4 K]

25. Find the value of the universal gas constant.
[**Ans.** R = $8{\cdot}31 \times 10^7$ ergs/per g mol. K]

26. Find the value of the ordinary gas constant for nitrogen.
[**Ans.** $r = 2{\cdot}97 \times 10^6$ ergs per g-K]

27. The resistance of a platinum resistance thermometer at the ice point is 5 ohms and at the steam point is 6·93 ohms. The pressure exerted by the gas in constant volume gas thermometer at the ice point is 100 cm of Hg and at the steam point it is 136·6 cm of Hg. When both the thermometers are placed in a bath, the resistance of a resistance thermometer is 5·795 ohms and the pressure of the gas is 114·9 cm of Hg. Calculate the Celsius temperature of the liquid (*i*) on the platinum scale and (*ii*) on the gas scale.
[**Ans.** $t_p = 41{\cdot}19$°C ; $\theta = 40{\cdot}71$°C]

28. The bulb of the Callendar's compensated constant pressure air thermometer is 800 cm^3. When the bulb is immersed in a bath, 200 cm^3 of mercury has to be drawn out of the reservoir. Calculate the temperature of the bath on the Celsius scale.
[**Ans.** 33·33°C]

29. If the platinum temperature corresponding to 60°C on the gas scale is 60·25°C, what will be the temperature on the platinum scale corresponding to 120°C on the gas scale ?
[**Ans.** 119·25°C]

30. If the platinum temperature corresponding to 60°C on the gas scale is 60·36°C, what is the platinum scale temperature corresponding to 151·7°C on the gas scale ? [**Ans.** 150°C]

2

Expansion

2·1 Introduction

All bodies change in size when they are heated. In general all bodies increase in size on heating except water (between 0°C and 4°C) and some aqueous solutions. This increase in the size of a body by heating or thermal expansion is present in solids, liquids and gases. In the case of solids, the increase will be in length, area or volume. In liquids and gases only expansion in volume is possible as they do not possess any fixed shape. In the case of gases, the state of a gas at any instant is dependent on its volume, pressure and temperature. Hence a gas can be heated at constant volume or at constant pressure. The property of thermal expansion of substances is different for different substances and it also depends on the state of the substance *viz* solid, liquid or gas. Thermal expansion is an important effect of heat and hence it has many practical applications. Construction of thermometers based on the property of expansion of liquids or gases is one of them, and this application has been discussed in the chapter on *Thermometry*. Some other applications of this property are discussed in this chapter.

2·2 Expansion of Solids

Solids can be divided into two categories (*i*) *isotropic* and (*ii*) *anisotropic*. Metals, glass and some regular systems of crystals come under isotropic solids These substances have the same properties in all directions and hence have the same coefficient of expansion in all directions. There are certain irregular crystals, which when heated expand in one direction and contract in a perpendicular direction. Hence their coefficient of expansion is different in different directions. They are called anisotropic bodies. The expansion of isotropic solids is discussed in this chapter.

2·3 Coefficient of Linear Expansion

The expansion of a solid can be in length, area or volume. Expansion in length is called linear expansion. As different bodies expand to different extents for the same rise of temperature, the property of linear expansion is denoted by a term called the *coefficient of linear expansion.* The coefficient of linear expansion of a body (designated as α) is defined as the increase in length per unit length per unit degree rise of temperature. If L_1 and L_2 are the lengths of a rod at temperatures t_1°C and t_2°C, then α the coefficient of linear expansion of the material is given by

$$\alpha = \frac{L_2 - L_1}{L_1(t_2 - t_1)}$$

$$\therefore \quad L_2 = L_1[1 + \alpha(t_2 - t_1)]$$

If L_0 and L_t refer to the lengths of the rod at 0°C and t°C, then

$$\alpha = \frac{L_t - L_0}{L_0 \times t}$$

or $$L_t = L_0(1 + \alpha t)$$

The equation, $L_t = L_0\,(1 + \alpha t)$ is applicable to the temperature range 0°C to 100°C. In this range, the expansion of the material can be taken to be uniform. For a wider range of temperature the length L_t at temperature t is given by the equation

$$L_t = L_0(1 + \alpha_1 t + \alpha_2 t^2 + \alpha_3 t^3 + \ldots)$$

where l_0 is the length of the rod at 0°C and α_1, α_2, α_3 etc. are coefficients of a rapidly decreasing order.

Since the values of α_2, α_3 etc. are very small, for all practical purposes the relation $L_t = L_0\,(1 + \alpha t)$ is used.

2 4 Coefficient of Superficial Expansion

It is defined as the increase in area per unit area per unit degree rise of temperature. If A_1 and A_2 are the areas of a solid at temperatures t_1 and t_2 then β the coefficient of superficial expansion is given by the relation

$$\beta = \frac{A_2 - A_1}{A_1(t_2 - t_1)}$$

If A_0 and A_t are the areas of a solid at 0 and t°C respectively then

$$\beta = \frac{A_t - A_0}{A_0 \times t}$$

or $$A_t = A_0(1 + \beta t)$$

2 5 Relation between α and β

Consider a square plate of side L_0 at 0°C and L_t at t°C.

Let the area of the plate be A_0 at 0°C and A_t at t°C

Then $$L_t = L_0\,(1 + \alpha t) \quad \ldots(i)$$

$$A_0 = L_0^2 \quad \ldots(ii)$$

$$A_t = L_t^2 \quad \ldots(iii)$$

and $$A_t = A_0(1 + \beta t) \quad \ldots(iv)$$

$$L_t^2 = L_0^2(1 + \beta t) \quad \ldots(v)$$

Substituting the value of L_t from equation (i) in (v)

$$L_0^2(1 + \alpha t)^2 = L_0^2\,(1 + \beta t)$$

or $$1 + 2\alpha t + \alpha^2 t^2 = 1 + \beta t$$

Neglecting the term α^2t^2,

$$2\alpha t = \beta t$$

$$\beta = 2\alpha$$

Thus the coefficient of superficial expansion of a substance is approximately twice its coefficient of linear expansion.

2·6 Coefficient of Cubical Expansion

The coefficient of cubical expansion is defined as the increase in volume per unit volume per unit degree rise of temperature. If V_1 and V_2 are the volumes of a substance at temperatures t_1 and t_2, then γ the coefficient of cubical expansion of the substance is given by

$$\gamma = \frac{V_2 - V_1}{V_1(t_2 - t_1)}$$

If V_0 and V_t are the values at 0°C and t°C respectively then

$$\gamma = \frac{V_t - V_0}{V_0 \times t}$$

or

$$V_t = V_0(1+\gamma t)$$

2·7 Relation between α and γ

Consider a cube of side L_0 at 0°C and L_t at t°C. Let the volume of the cube be V_0 at 0°C and V_t at t°C

Then

$$L_t = L_0(1+\alpha t) \qquad \text{...}(i)$$

$$V_0 = L_0^3 \qquad \text{...}(ii)$$

$$V_t = L_t^3 \qquad \text{...}(iii)$$

and

$$V_t = V_0(1+\gamma t) \qquad \text{...}(iv)$$

$$L_t^3 = L_0^3(1+\gamma t)$$

Substituting the value of L_t from equation (*i*) in (*iv*)

$$L_0^3(1+\alpha t)^3 = L_0^3(1+\gamma t)$$

or

$$1+3\alpha t+3\alpha^2t^2+\alpha^3t^3 = 1+\gamma t.$$

Neglecting the higher powers of α

$$3\alpha t = \gamma t$$

or

$$\gamma = 3\alpha$$

Thus the coefficient of cubical expansion is approximately three times its coefficient of linear expansion.

As a close approximation, the ratio between the three coefficients is

$$\alpha : \beta : \gamma = 1 : 2 : 3$$

As it is somewhat difficult to determine β and γ directly, for solids, the value of α is determined and the values of β and γ are taken approximately equal to 2α and 3α respectively.

2·8 Change of Density of a substance with Temperature

When a soild is heated its volume increases and consequently the density of the substance decreases.

Let m be the mass of a solid. Let v_1 and v_2 be the volumes of the soild at the temperatures t_1 and t_2°C. Let ρ_1 and ρ_2 be the corresponding densities. Then, since the mass of a solid remains constant at the two temperatures.

$$m = v_1\rho_1 = v_2\rho_2$$

$$\therefore \quad \frac{v_1}{v_2} = \frac{\rho_2}{\rho_1}$$

But $$v_1 = v_0(1+\gamma t_1)$$

and $$v_2 = v_0(1+\gamma t_2)$$

$$\therefore \quad \frac{v_2}{v_1} = \frac{1+\gamma t_2}{1+\gamma t_1}$$

or $$\frac{\rho_1}{\rho_2} = \frac{1+\gamma t_2}{1+\gamma t_1}$$

or $$\rho_1 = \rho_2[(1+\gamma t_2)(1+\gamma t_1)^{-1}]$$

$$= \rho_2[1+\gamma t_2-\gamma t_1] \text{ (neglecting the } \gamma^2 \text{ term)}$$

$$\rho_1 = \rho_2[1+\gamma(t_2-t_1)]$$

$$\rho_2\gamma(t_2-t_1) = \rho_1-\rho_2$$

or $$\gamma = \frac{\rho_1-\rho_2}{\rho_2(t_2-t_1)}$$

2·9 Coefficient of Linear Expansion (Spherometer Method)

This is the simplest method of determining the coefficient of linear expansion in the laboratory. The specimen whose coefficient of linear expansion is to be measured is taken in the form of a rod and its initial length (L_1) is measured at room temperature. The rod is placed in the linear expansion apparatus shown in Fig. 2·1 The lower end *B* of the rod rests against a fixed support and the upper end *A* is free to expand. The central screw of the spherometer is just above the end *A* of the rod. Initially, the central leg of the spherometer is rotated gently so that, it is just in contact with the upper end. The *just* position of contact can be judged with the help of an electrical circuit shown in the figure. The point of contact serves as the electrical switch and when the contact is made the bulb in the circuit glows The initial reading *a* of the spherometer is noted. Let the room temperature be t_1°C. The spherometer screw is slightly rotated up so that there is a gap for expansion of the end *A*.

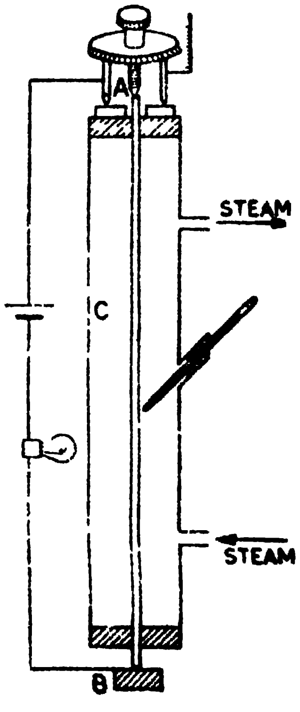


Fig. 2·1

Now steam is passed through the outer jacket *C* continuously till the temperature of the enclosure becomes constant and equal to the temperature of steam (t_2°C). After the steady state is reached, the spherometer screw is rotated down so that it comes in contact with the end *A* of the rod. Let this reading of the spherometer be *b*.

The coefficient of linear expansion α can be calculated as follows :

Initial length of the rod at temperature t_1°C = L_1
Initial temperature = t_1°C
Initial reading of the spherometer = a
Final temperature = t_2°C
Final reading of the spherometer = b
Increase in length = $(b-a)$
Coefficient of linear expansion

$$\alpha = \frac{\text{Increase in length}}{\text{Original length} \times \text{Change in temp.}}$$

$$= \frac{(b-a)}{L_1(t_2-t_1)} \text{ per °C}$$

This method can also be employed to measure the coefficient of linear expansion of a tube.

2·10 Optical Lever Method

This is a more sensitive method for determining the coefficient of linear expansion of the material of a rod in the laboratory. If the apparatus is rigid, this method can give very accurate values of α. This apparatus is the same as in the previous article except that the spherometer is replaced by an optical lever (Fig. 2·2).

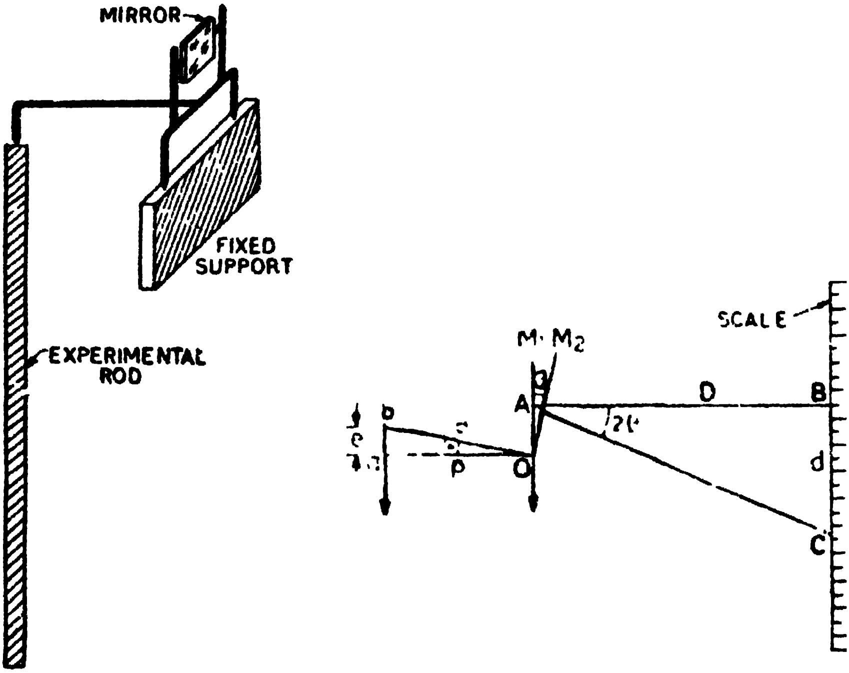


Fig. 2·2

The apparatus is shown in Fig. 2·2. The image of the scale in the mirror is viewed with a reading telescope Let the initial reading of the scale corresponding to the position of the horizontal cross-wires be d_1.

Now, steam is passed through the outer jacket till the temperature of the whole enclosure becomes constant and equal to the temperature of steam. Due to heating, the rod expands and consequently the leg of the optical lever resting on the rod is tilted up by a distance e, equal to the expansion of the rod. Let the mirror of the optical lever be rotated to the position OM_2 by an angle θ. Let the reading of the scale, when the temperature of the enclosure is constant, be d_2 When a mirror is rotated by an angle θ the reflected ray is rotated through 2θ.

$$\therefore \qquad \angle BAO = 2\theta$$

In the $\triangle Oab$,
$$\theta = \frac{ab}{p} = \tan\theta = \frac{e}{p}$$

where p is the perpendicular distance between the front legs and the hind leg.

In the $\angle$ BAC,

$$2\theta = \tan 2\theta = \frac{BC}{D} = \frac{d_2-d_1}{D} = \frac{d}{D}$$

(Here the angle θ is small and hence the tangent values can be taken equal to the angles). D is the distance between the mirror and the scale and $d = (d_2-d_1)$

$$\theta = \frac{e}{p} \text{ and } 2\theta = \frac{d}{D}$$

$$\therefore \qquad \frac{2e}{p} = \frac{d}{D} \quad \text{or} \quad e = \frac{pd}{2D}$$

Initial length of the rod at temperature t_1°C = L_1

Initial temperature = t_1°C

Final temperature = t_2°C

Increase in length $e = \frac{pd}{2D}$

∴ Coefficient of linear expansion

$$\alpha = \frac{\text{Increase in length}}{\text{Original length} \times \text{Change in temp.}}$$

$$= \frac{pd}{2DL_1\,(t_2-t_1)} \text{ per °C}$$

p the distance between the front legs and the hind leg is measured by taking the impressions of the legs on a sheet of paper.

The optical lever method is suitable to measure the coefficient of linear expansion of a material given in the form of a tube (Fig. 2·3). One end of the tube is fixed and the other end of the tube is free to expand. The optical lever is fixed over the free end as explained earlier. The tube is covered with cotton or felt so that heat is not lost to the surroundings. Observations are taken as explained earlier in this article and the value of the coefficient of linear expansion is calculated.

The coefficient of linear expansion of a rod or a tube can also be determined by using a screw gauge instead of a spherometer.

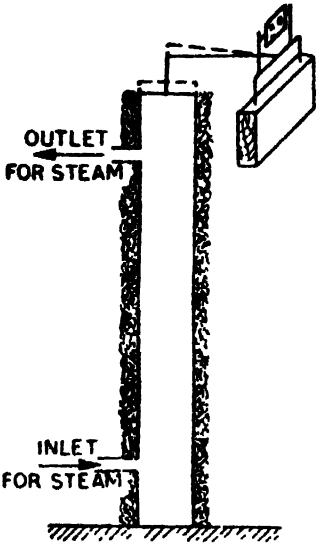


Fig. 2·3.

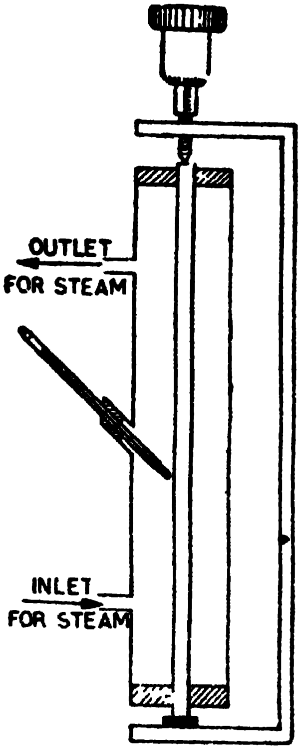


Fig. 2·4.

In this case, the reading of the screw gauge when it is in contact with the free end at the initial and final temperatures is noted and the difference between the two readings measures the expansion of the rod or tube (Fig. 2·4). Here the tip of the screw serves as the movable jaw and the free end of the rod as the fixed jaw of the screw gauge.

2·11 Comparator Method

The comparator method is very accurate for determining the coefficient of linear expansion of rods. The results obtained are of high precision. This method is used by the International Bureau of Weights and Measures for standardising measuring rods.

The method consists of comparing the length of an experimental rod maintained at a constant temperature with a standard rod maintained at the temperature of melting ice. The experimental rod is supported on two rollers and is kept inside a double walled vessel. The rod is surrounded by water and the temperature is maintained constant at any desired value with the help of a thermostat. The standard rod is supported in a similar vessel and the temperature of the standard rod is maintained constantly at 0°C. The two rods have fine scratches at the two ends approximately at a distance of one metre. The two vessels are supported on wheels capable of movement on two parallel rails fixed on a table. T_1 and T_2 are two microscopes fixed to two sturdy stone pillars P_1 and P_2. The two scratches can be viewed with the help of the microscopes. The microscopes themselves are capable of movement parallel to the length of the rod with the help of the micrometer screws M_1 and M_2 (Fig. 2 5). The vessels containing the rods can be brought under the microscopes one after the other. The microscopes are fitted with cross-wires.

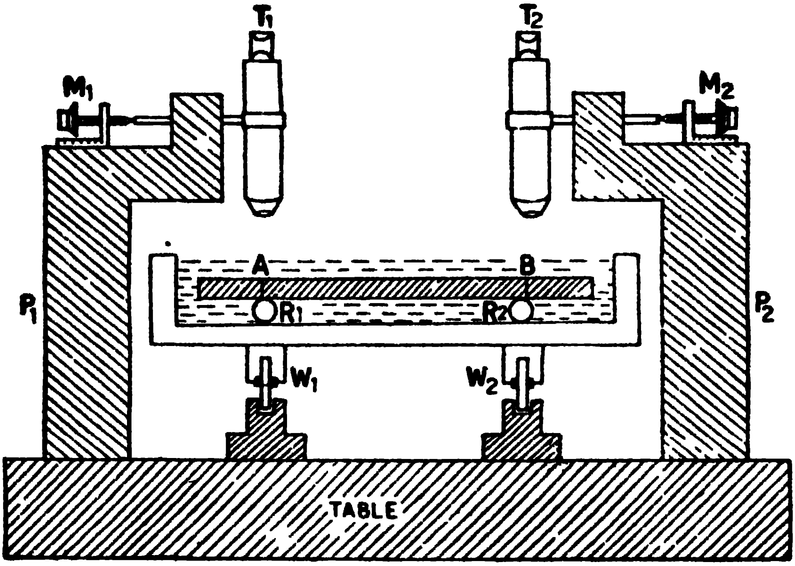


Fig. 2·5

Initially the readings of the micrometer screws when the cross wires are focussed on the scratches are noted with the standard rod first and then with the experimental rod, maintaining the temperatures of both at the temperature of melting ice. Then the experimental rod is maintained at the desired temperature and the readings are again noted at this constant temperature. Thus, the readings corresponding to the two scratches of experimental rod at different successive temperatures are observed. At the end, the standard rod is brought under the microscopes to check any displacement of the support during the experiment.

With the help of the observations mentioned above, it is possible to calculate the increase in length of the rod for different changes in temperature and the coefficient of linear expansion can be calculated in each case. This method also enables us to find the change in the length of the rod at different temperatures in comparison with the length of the standard rod at 0°C.

2·12 Henning's Tube Method

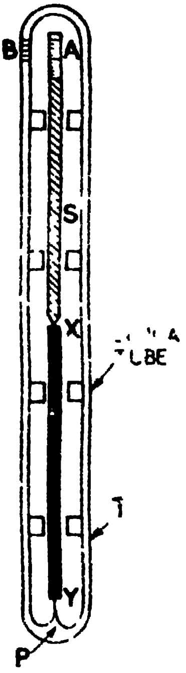


Fig. 2·6

This method is convenient to find the coefficient of linear expansion of the material of a rod accurately. The apparatus consists of a fused silica tube *T* having a pointed projection *P*. *XY* is the experimental rod, one end of which rests on the projection *P* and the other end is in contact with a fused silica rod *S*. The rod *XY* expands upwards and displaces the rod *S* upwards. The free end of the rod *S* carries a scale *O* engraved on the rod itself. *B* is another scale *A* engraved on the outer surface of the silica tube (Fig 2·6). The tube *T* is enclosed in a water bath and the level of water in the bath is up to about half the height of the rod *S*. The water bath is first maintained at a lower temperature and then at a higher temperature. The relative displacement of the scale *A* with respect to *B* as observed with a microscope, measures the expansion of the rod for the corresponding change in temperature. To determine the absolute value of the expansion of the rod, the expansion of silica is also taken into account. The expansion of silica for the temperature change under consideration can be obtained accurately by optical methods.

Coefficient of linear Expansion

Substance	$\alpha \times 10^6$ *per °C*
Quartz	0·4
Invar	0·9
Glass	4 to 9
Platinum	8·9
Steel	12
Gold	13·9
Copper	14
Silver	18·8
Brass	20
Aluminium	24
Zinc	26

2·13 Expansion of Crystals

In the case of isotropic bodies the coefficient of linear expansion is the same in all directions. The expressions derived earlier in this chapter refer only to isotropic bodies. In the case of anisotropic bodies like the crystals, the coefficient of expansion is ***different in different directions***. If a crystal is cut such that its faces are parallel to the three mutually perpendicular axes, then the coefficients of expansion of the crystal are different in the three directions. Let l, b and d the length, breadth and height of a crystal and α_1, α_2, and α_3 be its coefficients of expansion in the three directions. Let l', b' and d' be the dimensions of the crystal when its temperature is increased by t°C.

Then

$$l' = l(1+\alpha_1 t)$$

$$b' = b(1+\alpha_2 t)$$

and $$d' = d(1+\alpha_3 t)$$

Initial volume $V = lbd$

and final volume $V' = l'b'd'$

$$V' = l'b'd'$$

$$= lbd(1+\alpha_1 t)(1+\alpha_2 t)(1+\alpha_3 t)$$

$$= V\{1+(\alpha_1+\alpha_2+\alpha_3)t\}$$

taking only the terms of the first degree.

But $V' = V[1+\gamma t]$

where γ is the coefficient of cubical expansion of the crystal.

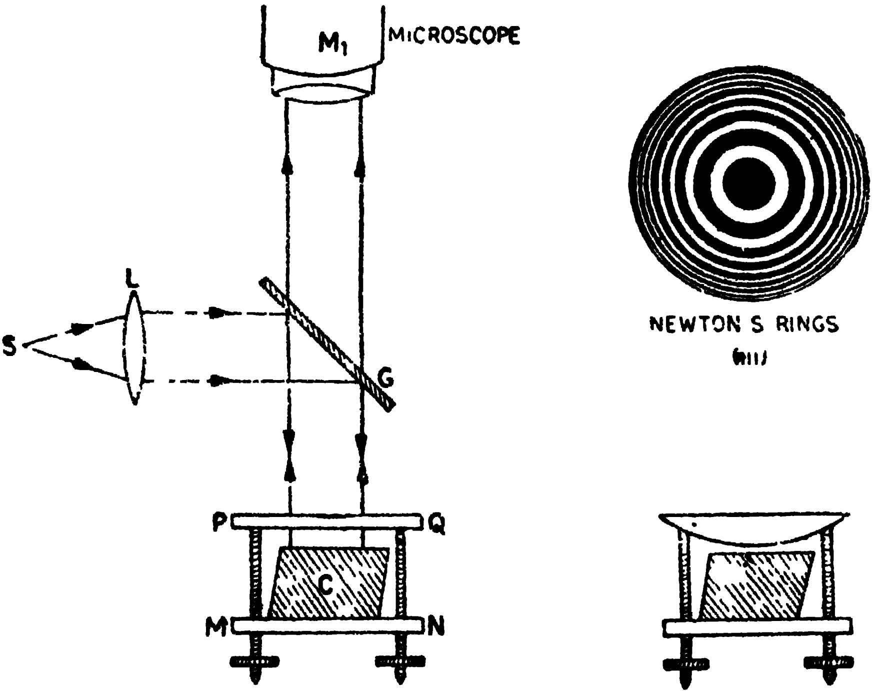
$$\therefore \quad \gamma = \alpha_1+\alpha_2+\alpha_3$$

Uniaxial crystals have an axis of crystalline symmetry and their physical properties are the same in a plane perpendicular to the axis of the crystal. Hence uniaxial crystals have only two coefficients of expansion. Negative coefficients of expansion are obtained with certain negative crystals However, it is observed that their coefficients of cubical (volume) expansion are positive.

2·14 Coefficient of Expansion of a Crystal (Fizeau's method)

This method is suitable to measure the expansion of small specimens *e.g.*, crystals. The experiment is based on the principle of interference of light.

The apparatus consists of a highly polished (plane) metal plate *MN*, which is supported on three metal screws passing through the plate. *PQ* is a smooth glass plate resting on the tips of the three screws (Fig. 2·7 The specimen (crystal) whose expansion is to be determined is placed on the plate *MN* and the screws are rotated such that the thickness of the air film between the upper surface of the crystal *C* and the lower surface of the glass plate *PQ* is very small. *S* is a monochromatic source of light, *L* is a condensing lens, *G* is a glass plate inclined at 45° to the path of the parallel beam of light from the lens and M_1 is a microscope fitted with cross wires. A parallel beam of light is incident on the glass plate *PQ* by this arrangement. Interference takes place due to the light reflected from the lower surface of *PQ* and the upper surface of the crystal. If these two surfaces are exactly parallel, the field of view just appears to be coloured without any fringes. But in practice it is not possible to have the two surfaces to be exactly parallel. A wedge shaped air film of very small angle is formed between the two surfaces *i.e.*, the thickness of the air film gradually changes from one point to the other of the crystal surface. This means that the path difference between the two reflected beams gradually increases. According to the theory of the colours of thin films viewed *by reflected light* any point in the field of view appears dark or bright depending on whether the path difference $2\mu T \cos r$ is even or odd multiples of $\lambda/2$. Here μ is the refractive index of air. T is the thickness of the air film, r is the angle of refraction and λ is the wavelength of light used.



(i) (ii)

Fig. 27

$$2\mu\, T \cos r = 2n\, \lambda/2 \quad \textit{dark}$$

$$2\mu\, T \cos r = (2n+1)\, \lambda/2 \quad \textit{bright}$$

But $\mu = 1$

and $r = 0$ for normal incidence

$\therefore$ $\cos r = 1$

$$2T = 2n\lambda/2 \qquad \text{dark} \qquad \ldots(i)$$

$$2T = (2n+1)\, \lambda/2 \qquad \text{bright} \qquad \ldots(ii)$$

As the thickness of the air film gradually changes, the interference pattern observed in the field of view consists of alternate bright and dark bands parallel to one another. The apparatus is enclosed in an outer bath and its temperature is maintained constant thermostatically at any desired value. The interference pattern is obtained and the cross wire is fixed on one of the dark bands. ***Now the temperature of the bath is gradually increased and the number of dark bands*** **(*p*)** ***that cross the field of view with reference to the cross wire is observed***, till the temperature becomes constant at the desired higher value and till no more fringes cross the field of view. The change in the thickness of the air film can be calculated as follows. If t_1 and t_2 are the thicknesses at the two temperatures, then from equation (*i*) above

$$T_1 = n\frac{\lambda}{2}$$

and
$$T_2 = (n-p)\frac{\lambda}{2}$$

or
$$T_1 - T_2 = p\frac{\lambda}{2} \qquad \ldots(iii)$$

where p is the number of fringes that cross the field of view. $(T_1 - T_2)$ measures the decrease in the thickness of the air film due to the expansion of the crystal and the expansion of the supporting legs between the plates *MN* and *PQ*. The increase in the thickness of the air film due to the expansion of the supporting legs alone can be determined separately for the same rise of temperature by removing the crystal and bringing the plates *MN* and *PQ* very near one another. Let the number of fringes that cross the field of view be p_1.

$$\text{Increase in the thickness of the air film} = \frac{p_1\lambda}{2}$$

$$\therefore \text{ Correct expansion of the crystal} = (p+p_1)\frac{\lambda}{2}$$

This gives the expansion of the crystal. Knowing the initial and final temperatures of the crystal and the thickness of the crystal in the direction of expansion, the coefficient of linear expansion of the crystal can be calculated.

$$\alpha_1 = \frac{(p+p_1)\frac{\lambda}{2}}{l_1(t_2-t_1)} = \frac{(p+p_1)\lambda}{2(l_1)(t_2-t_1)}$$

Here $(t_2 - t_1)$ is the change in temperature.

Similarly, the coefficients of expansion in the other two perpendicular directions also can be determined. If α_1, α_2 and α_3 are the coefficients of expansion in the three mutually perpendicular directions, then the coefficient of volume expansion γ is given approximately by $\gamma = \alpha_1 + \alpha_2 + \alpha_3$.

If the glass plate *PQ* is replaced by a plano-convex lens of large radius of curvature [Fig. 2·7 (*ii*)] the interference pattern consists of alternately bright and dark concentric rings called the Newton's rings system. When the temperature of the crystal is increased, the thickness of the air film at any point gradually decreases and the rings appear to expand outwards. With reference to the cross-wire on any particular dark ring, the number of dark rings (p) that cross the field of view is noted. Then the decrease in the thickness of the air film (T_1-T_2) is given by

$$T_1-T_2 = p\frac{\lambda}{2}$$

The displacement of one fringe is equal to a change in the thickness of the air film corresponding to half the wavelength of light used. Even a shift of $\frac{1}{5}$ of a fringe can be detected. If the wavelength of light used is 6000 Å $= 6\times10^{-5}$ cm, then a change in the thickness of air film equal to 6×10^{-6} cm can be detected. Thus the expansion of the crystal can be measured very accurately

The experiment is repeated for the same rise of temperature without the crystal. If p_1 is the number of rings that cross the field of view, then the increase in the thickness of the air film due to the expansion of the supporting legs $= p_1\lambda/2$.

The correct expansion of the crystal $= (p+p_1)\ \lambda/2$

Tutton's modification. Tutton modified the apparatus by placing the crystal over a small table having aluminium legs and resting on the plate MN, the supporting screws are made of platinum [Fig. 2·7 (a)].

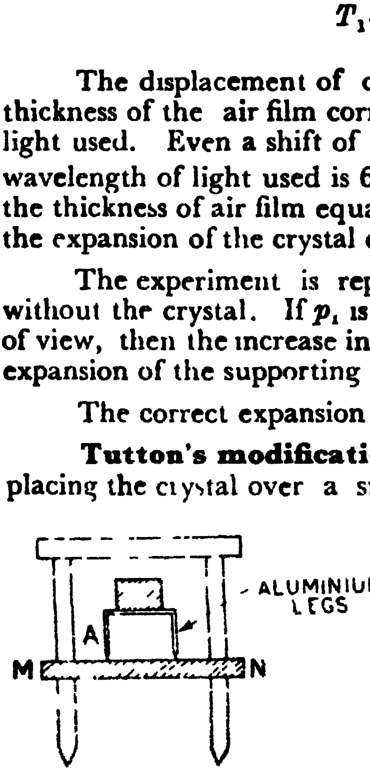


Fig. 2·7(a)

The height of the platinum screws and the height of the legs of aluminium are adjusted such that the increase in length is the same in the two cases. When the experiment is performed, the decrease in the thickness of the air film is only due to the expansion of the crystal

Let the number of fringes that cross the field of view be p

Increase in the length of the crystal $= p\ \lambda/2$

$$\therefore \qquad \alpha_1 = \frac{p\lambda}{2l_1(t_2-t_1)}$$

Example 2·1. *In Tutton's experiment for determining the coefficient of linear expansion of a crystal the following data was observed. Thickness of the crystal* = 1 cm, *wavelength of light used* = 5890×10^{-8} cm. *When the temperature of the crystal was increased from 20°C to 50°C, the number of fringes that crossed the field of view was 14. Calculate the coefficient of linear expansion of the crystal.*

Here $\lambda = 5890\times10^{-8}$ cm

$p = 14,\ l = 1$ cm

$t_2-t_1 = 50-20 = 30°C$

$$\alpha = \frac{p\lambda}{2l\,(t_2 - t_1)}$$

$$= \frac{14 \times 5890 \times 10^{-8}}{2 \times 1 \times 30}$$

$$= 13{\cdot}74 \times 10^{-6}/°C$$

2.15. Force due to Expansion or Contraction

The forces of expansion or contraction in metal rods and beams due to changes in temperature are very large. This is the reason why gaps are provided in the railway lines or in the rock pillars for bridges so as to allow for the expansion of the material in summer.

Consider a steel beam of length L metres. Assuming that this bar is subjected to a temperature change of 30°C, the increase in length of the bar

$$= L\,\alpha\,t$$

Here

$$\alpha = 12 \times 10^{-6} \text{ per °C}$$

and $$t = 30°C$$

Increase in length

$$= 12 \times 30 \times 10^{-6}\,L \text{ metres}$$

Strain produced in the beam

$$= \frac{\text{Increase in length}}{\text{Original length}}$$

$$= \frac{12 \times 30 \times 10^{-6} \times L}{L}$$

$$= 12 \times 30 \times 10^{-6}$$

According to Hooke's law (within the elastic limit)

$$Y = \frac{\text{Stress}}{\text{Strain}}$$

or

$$\text{Stress} = Y \times \text{Strain}$$

Young's modulus of elasticity of steel

$$= 2 \times 10^{12} \text{ dynes/sq cm}$$

$$\therefore \quad \text{Stress} = 2 \times 10^{12} \times 12 \times 30 \times 10^{-6} \text{ dynes/sq cm}$$

$$= 72 \times 10^{7} \text{ dynes/sq cm}$$

$$= 745 \text{ kg wt/sq cm}$$

If the bar has a cross-sectional area of 30 sq cm then the force due to the expansion of the specimen

$$= 745 \times 30$$

$$= 22{,}350 \text{ kg wt}$$

The force of expansion is independent of the length of the bar. If the bar is prevented from expansion or contraction, a force of magnitude calculated above will act on the bar. The force of contraction in metals due to increase in temperature has many useful applications. The boiler plates are riveted with red hot rivets and when the rivets cool, they produce steam proof joints. Shrinking of iron tyres on cart wheels is also done the same way.

Example 2·2. *A steel rod of length 5 metres is fixed rigidly between two supports. The coefficient of linear expansion of steel* $= 12 \times 10^{-6}/°C$. *Calculate the stress in the rod for an increase in temperature of 40°C. The Young's modulus of elasticity of steel* $= 2 \times 10^{12}$ dynes/sq cm.

Here

$$\alpha = 12 \times 10^{-6}/°\text{C},$$
$$Y = 2 \times 10^{12} \text{ dynes/sq cm}$$
$$t = 40°\text{C}$$
$$L = 500 \text{ cm}$$

Increase in length,

$$l = L\,\alpha\,t$$
$$\text{Strain} = \frac{l}{L}$$
$$= \frac{L\,\alpha\,t}{L}$$
$$= \alpha\,t$$
$$\text{Stress} = Y \times \text{Strain}$$
$$= Y\,\alpha\,t$$
$$= 2 \times 10^{12} \times 12 \times 10^{-6} \times 40$$
$$= 960 \times 10^{6} \text{ dynes/cm}^2$$

Example 2·3. *A steel wire 8 metres long and 4* mm *in diameter is fixed to two rigid supports. Calculate the increase in tension when the temperature falls by 10°C.*

$$\alpha = 12 \times 10^{-6}/°\text{C}$$
$$Y = 2 \times 10^{12} \text{ dynes/sq cm}$$

Here

$$\alpha = 12 \times 10^{-6}/°\text{C}$$
$$Y = 2 \times 10^{12} \text{ dynes/sq cm}$$
$$t = 10°\text{C}$$
$$L = 800 \text{ cm}$$
$$r = 0{\cdot}2 \text{ cm}$$

Increase in length, $l = L\,\alpha\,t$

Strain $= \dfrac{l}{L} = \dfrac{L\,\alpha\,t}{L} = \alpha t$

Stress $= Y \times \text{Strain}$

$= Y\,\alpha\,t$

Area of cross-section $= \pi r^2$

Increase in tension $=$ stress × area of cross-section

$= Y\,\alpha\,t \times \pi r^2$ dynes

$$= \frac{2 \times 10^{12} \times 12 \times 10^{-6} \times 10 \times 22 \times 0{\cdot}2 \times 0{\cdot}2}{7}$$

$= 30{\cdot}17 \times 10^6$ dynes

Example 2·4. *A uniform rod of 2* sq mm *cross-section is heated from 0°C to 20°C. Find the force which must be exerted to prevent it from expanding. Find also the energy stored per unit volume.* $\alpha = 12 \times 10^{-6}/°C$ *and* $Y = 10^{11}$ newtons/sq metre.

Here $\alpha = 12 \times 10^{-6}/°C$,

$Y = 10^{11}$ newtons/sq metre

$t = 20°C$, $a = 2$ sq mm

$= 2 \times 10^{-6}$ sq metre

Increase in length, $l = L\,\alpha\,t$

Strain $= \dfrac{l}{L} = \dfrac{L\,\alpha\,t}{L} = \alpha t$

Stress $= Y \times \text{Strain} = Y\,\alpha\,t$

Force $=$ Stress × area of cross-section

$= Y\,\alpha\,t \times a$

$= 10^{11} \times 12 \times 10^{-6} \times 20 \times 2 \times 10^{-6}$

$=$ **48 newtons**

Energy stored per unit volume $= \dfrac{1}{2} \times$ stress × strain

$$= \frac{1}{2} \times Y\,\alpha t \times \alpha t$$

$$= \frac{10^{11} \times (12 \times 10^{-6})^2 \times (20)^2}{2}$$

$=$ **2880 j/m³.**

Example 2·5. *A steel wire of diameter 1* mm *supports a load which is sufficient to keep the wire taut at 20°C. Calculate the additional load that will be required to restore the length of the wire to its initial value when the temperature falls to* 0°C.

$y = 2 \times 10^{11}$ newtons/sq metre

$$\alpha = 10^{-6}/^\circ\mathrm{C},\ \text{diameter} = 1\ \text{mm} = 10^{-3}\ \text{metre}$$

$$\text{Area of cross-section } a = \frac{\pi d^2}{4} = \frac{22\times10^{-6}}{28}\ \text{sq metre}$$

$$\text{Decrease in length} = L\,\alpha\,t$$

$$\text{Strain} = \frac{L\,\alpha\,t}{L} = \alpha t$$

$$\text{Stress} = Y\times\text{Strain} = Y\,\alpha\,t$$

Force required to maintain the original length

$$= \text{Stress}\times\text{area of cross-section}$$

$$= y\,\alpha\,t\times a$$

$$= \frac{2\times10^{11}\times12\times10^{-6}\times20\times22\times10^{-6}}{28}\ \text{newtons}$$

$$= \frac{44\times6}{7\times9{\cdot}8}\ \text{kg wt}$$

$$= \mathbf{3{\cdot}847\ kg\ wt}$$

2·16 Expansion of Liquids

When a liquid is heated, its volume changes. Liquids have no shape of their own but conform to the shape of the containing vessel. When a liquid is heated, the containing vessel also expands and hence the measured increase in volume of the liquid is the apparent increase in volume. The real increase in volume of the liquid is equal to the sum of the apparent increase in volume of the liquid and the increase in volume of the containing vessel. Thus, a liquid has two coefficients of expansion, γ_a and γ_r called the coefficients of apparent and real expansion of the liquid respectively.

The coefficient of apparent expansion of a liquid (γ_a) is defined as the apparent increase in volume per unit volume per unit degree rise in temperature when the liquid is heated in a vessel that expands with heating.

The coefficient of real expansion of a liquid (γ_r) is defined as the actual increase in volume per unit volume per unit degree rise in temperature.

The expansion of most of the liquids is irregular except mercury whose expansion is uniform. Due to the irregular expansion of liquids, two coefficients of expansion called the *zero coefficient* and the *mean coefficient* are used. Zero coefficient is the increase in volume per unit volume at 0°C per unit degree rise of temperature. If V_0 and V_t are the volumes of a liquid at 0°C and t°C respectively, then the zero coefficient is given by

$$\gamma = \frac{V_t - V_0}{V_0\times t}$$

If V_1 and V_2 are the volumes of a liquid at t_1°C and t_2°C respectively then the mean coefficient of expansion is given by

$$\gamma = \frac{V_2 - V_1}{V_1\,(t_2 - t_1)}$$

2·17 Relation between γ_r and γ_a

Consider a liquid contained in a graduated vessel which reads the volume correctly at 0°C. Let V_0 and V_1 be the volumes of the liquid at 0°C and t°C. Then the coefficient of apparent expansion of the liquid is given by

$$\gamma = \frac{V_1 - V_0}{V_0 t} \text{ or } \frac{V_1}{V_0} = (1+\gamma_a t)$$

If γ_g is the coefficient of cubical expansion of the containing vessel, then the real volume of the vessel at t°C corresponding to a reading V_1 will be given by $V_1[1+\gamma_g t]$

Hence the coefficient of real expansion of the liquid is given by

$$\gamma_r = \frac{V_1[1+\gamma_g t] - V_0}{V_0 t}$$

$$= \frac{V_1 - V_0}{V_0 t} + \frac{V_1}{V_0}\cdot\gamma_g$$

$$= \gamma_a + (1+\gamma_a t)\gamma_g$$

$$= \gamma_a + \gamma_g + \gamma_a \gamma_g t$$

Neglecting the term $\gamma_a \gamma_g t$,

$$\gamma_r = \gamma_a + \gamma_g$$

Thus, the coefficient of real expansion of a liquid is approximately equal to the sum of the coefficient of apparent expansion of the liquid and the coefficient of cubical expansion of the containing vessel. If α_g is the coefficient of linear expansion of the material of the containing vessel $\gamma_g = 3\alpha_g$ (approximately).

2·18 Determination of γ_a with a Dilatometer

A dilatometer consists of a glass bulb attached to a stem. The stem is calibrated to read the volume directly (Fig 2.8). The dilatometer method is suitable to measure the mean coefficient of apparent expansion of a liquid over different ranges of temperature. The volumes of the liquid V_0 and V_t at 0°C and t°C are noted and γ_a is calculated from the formula

$$\gamma_a = \frac{V_t - V_0}{V_0 t}$$

The dilatometer method is most suitable for finding the coefficient of expansion of volatile liquids

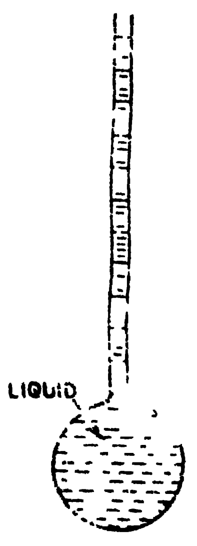


Fig 2.8

2·19 Determination of γ_a by weight thermometer Method

The weight thermometer consists of an elongated glass or fused silica bulb fitted with a narrow glass tube bent twice at right angles (Fig. 2·9). The mass of the empty dry weight thermometer is initially determined (W_1 g). Now the weight thermometer is filled with the given liquid at 0°C by alternate heating and cooling. The mass of the thermometer when it is filled with the liquid is determined (W_2 g). The mass of the liquid filling the whole bulb at 0°C is given by $M_0 = (W_2 - W_1)$. If ρ_0 is the density of the liquid at 0°C, then the initial volume of the liquid

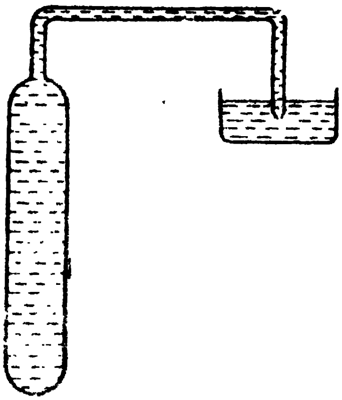


Fig. 2·9

$$= V = \frac{M_0}{\rho_0}$$

Now the weight thermometer is heated in a bath to a constant high temperature (t°C) say the boiling point of water. Due to the expansion, the liquid overflows and when the expansion is complete, the bulb is removed from the bath and is cooled. The mass of the weight thermometer and the liquid left behind is noted (W_3 g). Mass of the liquid left behind $M_1 = W_3 - W_1$.

Volume of this liquid

$$V_0 = \frac{M_1}{\rho_0}$$

This means that a volume V_0 of the liquid at 0°C when heated to t°C occupies a volume V viz., the complete volume of weight thermometer. Therefore, the coefficient of apparent expansion of the liquid is given by

$$\gamma_a = \frac{\text{Increase in volume}}{\text{Original volume} \times \text{Change in temperature}}$$

$$\gamma_a = \frac{\frac{M_0}{\rho_0} - \frac{M_1}{\rho_0}}{\frac{M_1}{\rho_0} \times t}$$

$$\gamma_a = \frac{M_0 - M_1}{M_1 \times t}$$

(But $M_0 - M_1$ is the mass of the liquid expelled and M_1 is the mass of liquid left behind).

$$\therefore \quad \gamma_a = \frac{\text{Mass of the liquid expelled}}{\text{Mass of the liquid left behind} \times \text{rise in temperature}}$$

In the laboratory, a specific gravity bottle may also be used to determine the coefficient of apparent expansion of a liquid.

To find the coefficient of real expansion of the liquid, the coefficient of cubical expansion of the vessel is found from the constant tables

Then $\gamma_r = \gamma_a + \gamma_g$.

2·20 Determination of the Coefficient of Real Expansion of a Liquid by Dulong and Petit's Method

Dulong and Petit carried out the first direct determination of the coefficient of real expansion of a liquid in 1817. The apparatus consists of a long glass tube *ABCDEFGH* bent in the shape shown in Fig. 2·10. The tube contains the liquid whose coefficient of real expansion has to be determined. The vertical limbs *CD* and *EF* are surrounded by two outer jackets. Through the jacket of *CD*, steam is passed and through the jacket of *EF* cold water is circulated. Let the temperatures of the cold and the hot limbs be t_1°C and t_2°C respectively. The horizontal limb *DE* is trapped with a piece of cloth and cold water is poured over it continuously so that there is no conduction of heat from the hot to the cold limb. When the temperatures in the two limbs are constant the liquid in the projecting limbs *AB* and *GH* stands at constant levels. The difference in levels between the two limbs can be determined. As the points *D* and *E* are at the same horizontal level, the pressure at *E* = the pressure at *D*. Let h_1 and h_2 be the heights of the liquid columns and ρ_1 and ρ_2 the densities of the liquid at temperatures t_1°C and t_2°C respectively.

Pressure at *E* = Pressure at *D*

$$P_A + h_1\rho_1 g = P_A + h_2\rho_2 g$$

where P_A is the atmospheric pressure

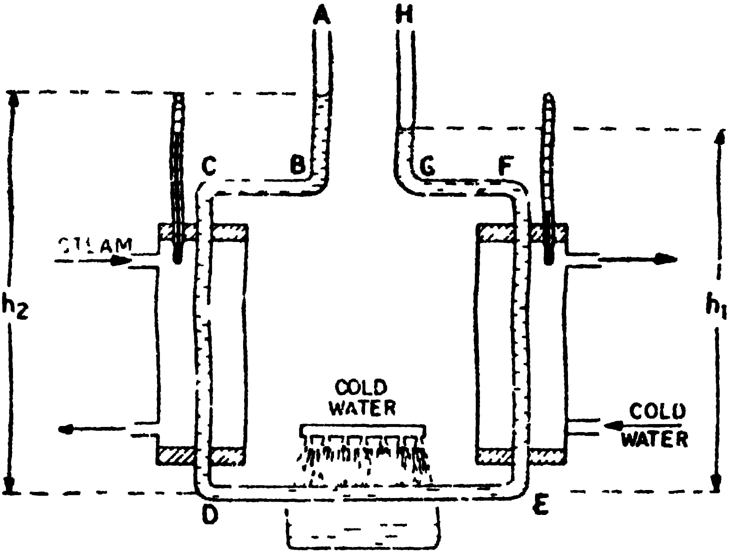


Fig. 2·10

or $$\frac{h_1}{h_2} = \frac{\rho_2}{\rho_1}$$

But $$\rho_0 = \rho_1(1+\gamma_r t_1)$$

and $$\rho_0 = \rho_2(1+\gamma_r t_2)$$

$$\therefore \quad \frac{\rho_2}{\rho_1} = \frac{1+\gamma_r t_1}{1+\gamma_r t_2}$$

$$\therefore \quad \frac{h_1}{h_2} = \frac{1+\gamma_r t_1}{1+\gamma_r t_2}$$

$$h_1+h_1\gamma_r t_2 = h_2+h_2\gamma_r t_1$$

$$\gamma_r(h_1t_2-h_2t_1) = h_2-h_1$$

or $$\gamma_r = \frac{h_2-h_1}{h_1t_2-h_2t_1}$$

In the original experiment of Dulong and Petit, the cold limb is surrounded by melting ice and the hot limb is surrounded by an oil bath heated by a furnace. The temperatures are measured with the help of an air thermometer. Heights h_1 and h_2 are measured using a cathetometer. γ_r is calculated on the basis of the pressure of the liquid column which is dependent on the height of the liquid column and the density of the liquid at that temperature. It is not dependent on the volume of the liquid. Hence the value of γ_r obtained from this method measures the coefficient of real expansion of the liquid. It is necessary that the projections *AB* and *GH* of the glass tube above the level of the jackets are small.

This simple arrangement has the following sources of error : (*i*) Convection currents along the horizontal tube *DE* and the necessity of the projecting portions *AB* and *GH* result in unequal heating of the liquid. (*ii*) As the two limbs *AB* and *GH* are widely separated, the difference in levels h_2-h_1 cannot be accurately determined. (*iii*) As the temperature of the two limbs is different, the effect of surface tension on the two liquid surfaces will be different. The error due to this is minimised by using tubes of wider bore, but this again means smaller value of h_2-h_1.

2·21 Regnault's Modification of Dulong and Petit's Method (First Method)

To avoid the errors in the Dulong and Petit's method, Regnault modified the experiment in two ways. In the first experiment, the arrangement consists of a U-tube *ABCD* consisting of two vertical limbs *AB* and *CD* of wide bore. The two tubes are connected at the top by a glass tube having a hole at *E*. This will enable the pressure over the surface of liquid to be equal to the atmospheric pressure. The lower ends of the limbs are connected by a horizontal tube and an inverted U-tube as shown in Fig. 2·11. Pressure is applied through the tube *G*. Initially when the temperature of the limbs is the same, liquid stands at the same height in the limbs of the inverted *U*-tube. The vertical limb *AB* is maintained at the higher temperature and the limb CD and the inverted U-tube are kept cold. The temperature of the hot limb is measured with an air thermometer.

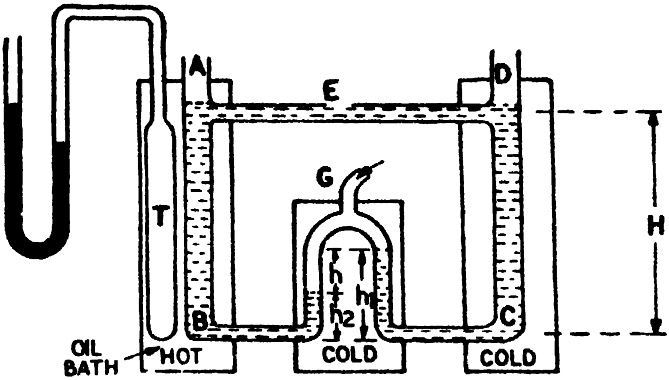


Fig. 2·11

When the temperatures of the limbs are constant, the heights h_1 and h_2 are noted. Let ρ_0 and ρ_t be the densities of the liquid in the cold and the hot limbs respectively. Let P be the excess of pressure in the inverted U-tube above the atmospheric pressure.

Then for the hot limb

$$P = H\rho_t - h_2\rho_0$$

and for the cold limb

$$P = H\rho_0 - h_1\rho_0$$

$$\therefore \quad H\rho_t - h_2\rho_0 = H\rho_0 - h_1\rho_0$$

$$H\rho_0 - H\rho_t = (h_1 - h_2)\,\rho_0$$

$$\rho_0\,[H-(h_1-h_2)] = H\rho_t$$

$$\frac{\rho_0}{\rho_t} = \frac{H}{H-(h_1-h_2)}$$

But

$$\frac{\rho_0}{\rho_t} = (1+\gamma t)$$

$$\therefore \quad \frac{H}{H-(h_1-h_2)} = 1+\gamma t$$

$$\gamma = \frac{h_1-h_2}{[H-(h_1-h_2)]t} = \frac{h}{(H-h)t}$$

Knowing H, h and t, γ can be calculated.

2·22 Regnault's Modification of Dulong and Petit's Method (Second Method)

In the second method due to Regnault, the experimental arrangement consists of two glass tubes $ABCD$ and $EFGH$ joined by a flexible iron tubing DE (Fig. 2·12). The tubes CB and GF are narrow. The projecting limbs AB and GH are maintained at a constant temperature t_2; the vertical limb CD is maintained at a high temperature t_1; the vertical limb *EF* is maintained at a temperature t_3; and the connecting limb *DE* is exposed to air and let this temperature be t_4. The tubes *BC* and *GF* are adjusted to be accurately horizontal. When the temperatures are constant, let the heights of the mercury columns be h_1, h_2, h_3, H_1 and H_2 in the limbs *AB*, *GH*, *ED*, *CD* and *EF* respectively. If ρ_1, ρ_2 etc. are the densities of the liquid at the temperatures t_1, t_2 etc. then the pressures at *D* due to the columns of mercury in the hot and the cold limbs must be equal.

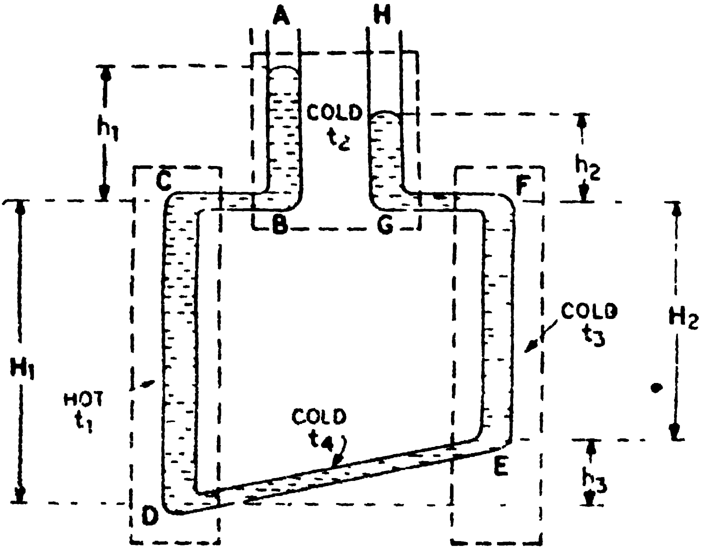


Fig. 2.12

$$\therefore \quad h_1\rho_2 + H_1\rho_1 = h_2\rho_2 + H_2\rho_3 + h_3\rho_4$$

But
$$\rho_1 = \frac{\rho_0}{1+\gamma t_1}$$

$$\rho_2 = \frac{\rho_1}{1+\gamma t_2}$$

$$\rho_3 = \frac{\rho_0}{1+\gamma t_3}$$

and
$$\rho_4 = \frac{\rho_0}{1+\gamma t_4}$$

$$\therefore \quad \frac{h_1}{1+\gamma t_2} + \frac{H_1}{1+\gamma t_1} = \frac{h_2}{1+\gamma t_2} + \frac{H_2}{1+\gamma t_3} + \frac{h_3}{1+\gamma t_4}$$

or
$$\frac{h_1-h_2}{1+\gamma t_2} + \frac{H_1}{1+\gamma t_1} = \frac{H_2}{1+\gamma t_3} + \frac{h_3}{1+\gamma t_4}$$

The heights and the temperatures are known in the above equation. Hence the value of γ can be calculated. The temperature t_4 is not accurately known. But this does not involve appreciable error because the height h_3 is very small.

2·23. Experiment of Callendar and Moss

In the second method of Regnault described in Art 2 22, the total length of the liquid column was 1·5 metres. Callendar and

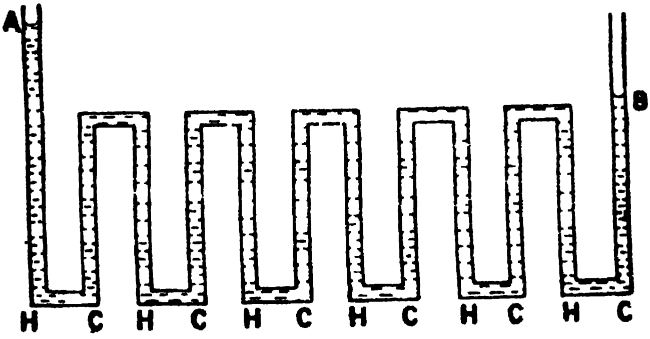


Fig. 2 13 (*a*)

Moss modified the experiment by using six hot and six cold limbs arranged in series [Fig 2 13 (*a*)] and each limb had a length of 2 metres. This will mean that the difference in levels of the liquid in the projecting limbs will be eight times approximately. The hot columns are arranged side by side and enclosed in a constant temperature bath. Similarly all the cold columns are arranged side by side [Fig. 2·13 (*b*)].

With this experimental arrangement Moss was able to find the absolute coefficient of expansion of mercury from 0°C to 300°C.

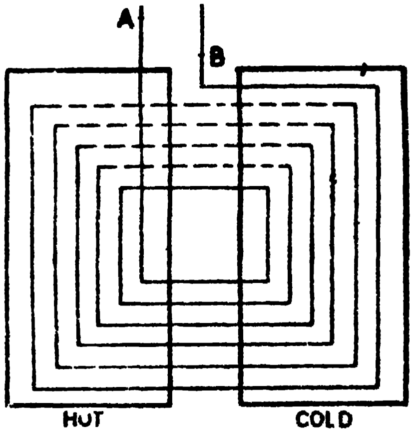


Fig. 2·13 (*b*).

Coefficient of cubical Expansion

Substance	$\gamma_r \times 10^3$ per °C
Mercury	0·182
Glycerine	0·485
Ethyl Alcohol	0·745
Petroleum	0·899
Turpentine	0·940
Carbon disulphide	1·140
Water 5°C to 10°C	0·053
Water 10°C to 20°C	0·150
Water 20°C to 40°C	0·302

2·24 Anomalous Expansion of Water

Most of the liquids expand uniformly over moderate ranges of temperature except water. Water shows a marked exception when it is heated from 0°C to 10°C, initially it contracts in volume up to 4°C, its volume is minimum at 4°C and beyond 4°C the volume increases. A graph between volume and temperature is shown in Fig 2·14.

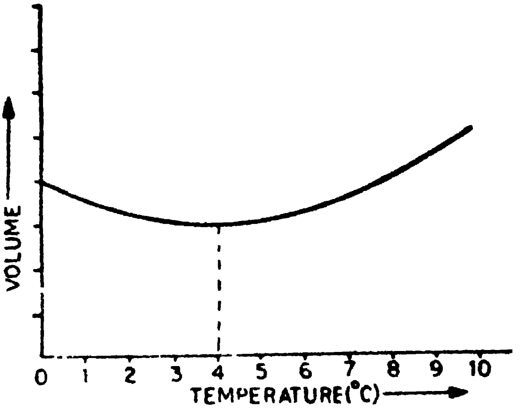


Fig. 2·14

The variation in the volume of water can be studied with a volume dilatometer. It consists of a glass bulb fitted with a narrow graduated glass tube. The bulb is filled to 1/7th of its volume with mercury so as to compensate for the expansion of the bulb. A fixed volume of water is taken in the bulb at 0°C and its volume is noted at various temperatures up to 10°C. The graph shows that the volume is minimum at 4°C. It means water possesses maximum density at 4°C.

Hope's Experiment. The apparatus consists of a cylindrical jar containing water and surrounded by a jacket containing ice in the middle of the jar as shown in Fig. 2·15. T_1 and T_2 are two thermometers to record the temperatures of water below and above the jacket respectively.

Water at 10°C is taken in the jar and the temperature shown by the thermometers T_1 and T_2 are recorded after equal intervals of time (say ½ minute).

A graph between temperature along the y-axis and time along the x-axis is plotted. The graphs for the two thermometers are as shown in Fig. 2·16.

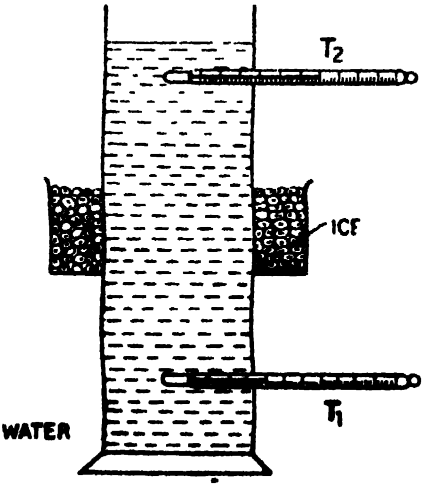


Fig. 2·15

The thermometer T_1 shows a sudden fall of temperature up to 4°C. The thermometer T_2 shows a slow fall in temperature When the temperature of T_1 remains at 4 C, the temperature T_2 falls rapidly. Then thermometer T_2

records a temperature of 0°C first and the thermometer T_1 afterwards. The point of intersection of the two curves gives the temperature of maximum density.

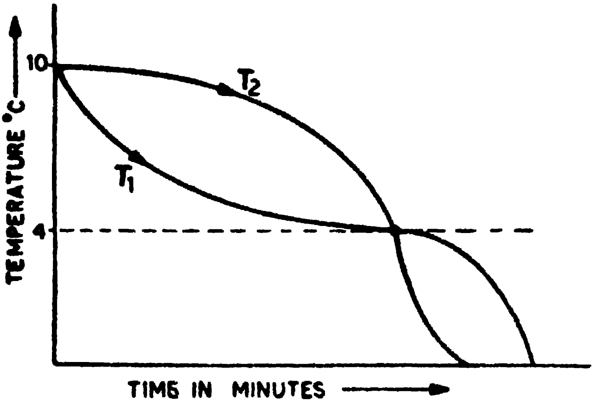


Fig. 2·16

When water in the middle of the jar is cooled by ice, its density increases and the heavier layers move down. Due to this reason the temperature of T_1 shows rapid fall in the beginning. When the temperature of water in the lower portion of the jar is 4°C, its density is maximum. When water in the middle cools to a temperature below 4°C, its density decreases and these layers move upwards. Due to this reason the thermometer T_2 shows a rapid fall of temperature. When the upper layers have attained a temperature of 0°C, the lower layers start cooling below 4°C.

The temperature of maximum density of water has been found by Joule and Playfair. By a series of experiments they found the temperature of maximum density of water to be 3·95°C.

With the increase in pressure over water the temperature of maximum density of water decreases

$$t_{max} = [3{\cdot}98 - 0{\cdot}0225\,(P-1)]°\mathrm{C}$$

where P is the pressure in atmospheres. According to this relation, 1 kg of water has a volume of 1000 028 cc at 4°C.

Thus 1 cc of water at 4°C has a mass not exactly equal to 1 gram. Therefore a standard kg cannot be taken as the mass of 1 cubic decimetre of water (1000 cc) at 4°C. But it is defined in terms of a prototype kg made of platinum-iridium alloy.

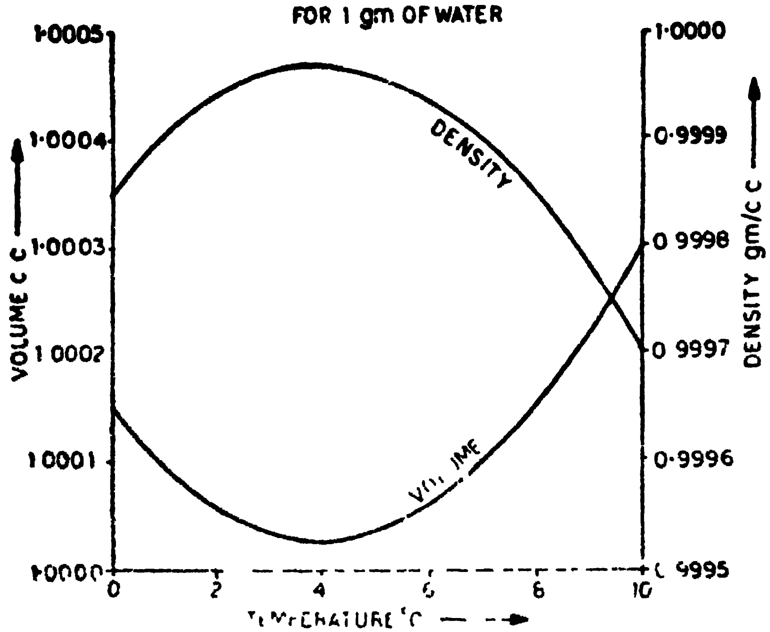


Fig. 2·16 (a)

Density of water at various temperatures

Temperature °C	Density g/cc	Volume of 1 gram of water (cc)
0	0·99987	1·00013
2	0·99997	1·00003
4	1·00000	1·00000
6	0·99997	1·00003
8	0·99988	1·00012
10	0·99973	1·00027
20	0·99823	1·00177
30	0·99567	1·00433
40	0·99220	1·00790
50	0·98810	1·01200

2·25. Thermostats

A thermostat is a device used to maintain the temperature of a water bath or an oven at constant temperature.

Toluene Thermostat. A liquid thermostat consists of an elongated glass bulb *A* which contains a liquid having high coeffi-

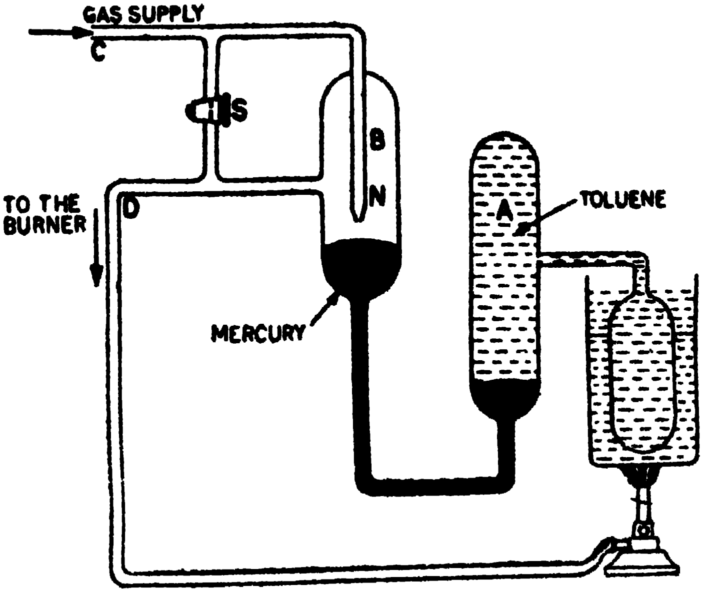


Fig. 2·17

cient of expansion *e.g.*, toluene or alcohol. The bulb *A* is connected to another bulb *B* through a glass tubing as shown and the connecting tube and also partly bulbs *A* and *B* contain mercury. Mercury is in contact with the expansible liquid in *A* and is almost up to the nozzle in *B*. The gas supply is connected at *C* and the burner is connected at *D*. *S* is a stop cock used for regulating the supply of gas from *C* to *D* (Fig. 2·17) The bulb is immersed in the water bath and when the temperature of the bath increases, toluene expands and pushes mercury down. Consequently the level of mercury in *B* rises and when the desired temperature is reached, the gas supply to the burner through the nozzle is cut off. The stop-cock *S* helps to maintain a feeble supply of the gas so that the burner is not put off. When the gas supply is considerably cut off, the temperature of the bath decreases, toluene contracts and the level of mercury in *B* goes down. Thus the gas supply to the burner through the nozzle is restored and the temperature of the bath increases again. The process repeats and the temperature of the liquid thermostat is limited by the boiling point of the liquid. In the case of toluene, this temperature is 111°C.

Bimetallic Thermostat. For higher temperature control bimetallic thermostats are used. The bimetallic strip works as an electric contact breaker in an electrical heating circuit. The circuit is broken when the desired temperature of the bath is reached. Due to the difference in the coefficients of linear expansion of the two metals, when it is heated the metallic strip curves and the circuit is broken. The metal of higher coefficient of expansion (say brass) bends more than the other of lesser coefficient of expansion say (invar steel). In Fig. 2·18 (*a*) the metallic strip is in contact

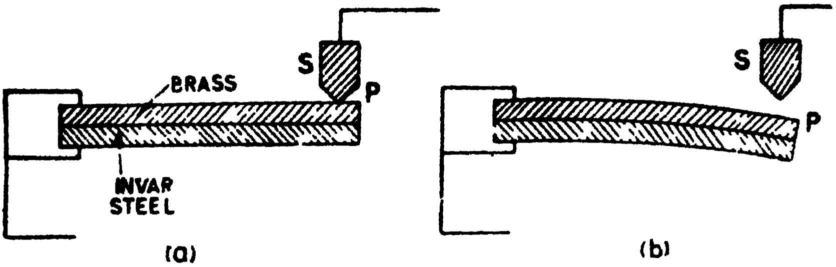


Fig. 2·11

with the screw *S* and in Fig. 2·18 (*b*) due to heating the strip curves downwards and the contact at *P* is broken and the current through the heating coil stops. When the temperature falls, the strip contracts and the contact at *P* is restored. The two metal strips are well riveted.

2·26 Expansion of Gases

A gas can be heated at constant pressure or at constant volume. Hence there are two coefficients of expansion for a gas *viz.*, the pressure coefficient and the volume coefficient.

Pressure coefficient (γ_p) is defined as the increase in pressure per unit pressure per unit degree rise of temperature at constant volume. If P_0 and P_t are the pressures of a given mass of gas at temperatures 0°C and t°C respectively, then

$$\gamma_p = \frac{P_t - P_0}{P_0 \times t} \quad \text{(at constant volume)}$$

or

$$P_t = P_0 [1 + \gamma_p t]$$

Volume coefficient (γ_v) is defined as the increase in volume per unit volume per unit degree rise of temperature at constant pressure. If V_0 and V_t are the volumes of a given mass of gas at temperatures 0°C and t°C respectively, then

$$\gamma_v = \frac{V_t - V_0}{V_0 \times t} \quad \text{(at constant pressure)}$$

or

$$V_t = V_0 [1 + \gamma_v t]$$

Study of the properties of expansion of gases is as important as the study of the expansion of liquids and solids. The property of expansion of a gas has provided an accurate and standard method of measuring temperature (*vide* chapter 1 on thermometry). Further, the properties of expansion of gases has led to the deduction of the universal gas laws.

The expansion of gases is much more than liquids and the expansion of the container is very small.

2·27 Determine of the Pressure Coefficient of a Gas

The apparatus consists of a glass bulb *B* connected to a glass tube bent twice at right angles. This tube is connected to a reservoir *R* containing mercury through a rubber tubing (Fig. 2·19). The bulb *B* is filled with mercury to approximately $\frac{1}{7}$th of its volume so as to compensate for the expansion of the bulb. The bulb is kept in a bath and the temperature of the bath can be kept constant at any desired value.

Initially the bulb is maintained at the temperature of melting ice and the pressure P_0 of the gas is determined at 0°C. Now the bulb is maintained at different temperatures t_1°C, t_2°C etc. and the pressures of the gas P_1, P_2 etc. are calculated at each temperature. Before noting the difference in levels at any temperature, the level of mercury in the closed limb is brought to the fixed mark *M* so that the volume of the gas is kept constant at each temperature.

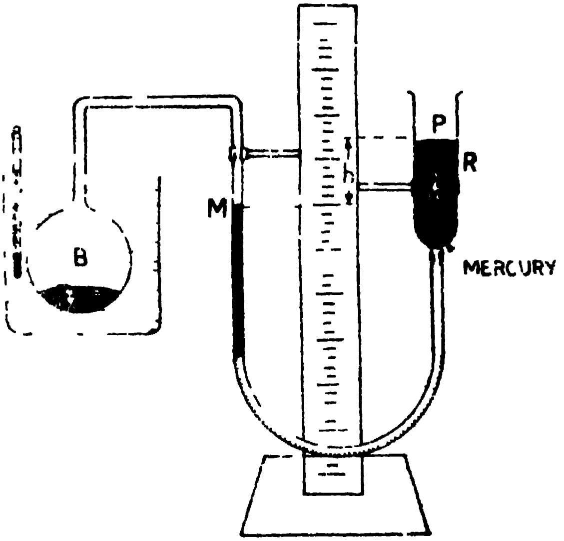


Fig. 2·19

If h_0, h_1, h_2 etc. are the differences in levels at 0 C, t_1°C, t_2°C etc. and P_A is the atmospheric pressure, then

$$P_0 = P_A \pm h_0\ ;$$

$$P_1 = P_A \pm h_1\ ;$$

$$P_2 = P_A \pm h_2 \text{ etc.}$$

according as the level of mercury in *R* is above or below the fixed mark *M*. Then

$$\gamma_p = \frac{P_1 - P_0}{P_0 \times t_1} = \frac{P_2 - P_0}{P_0 \times t_2} \text{ etc.}$$

The value of γ_p is calculated in each case and the mean value is taken.

If a graph is drawn between temperature in °C along the X-axis and the pressure of the gas along the Y-axis, the graph will be a

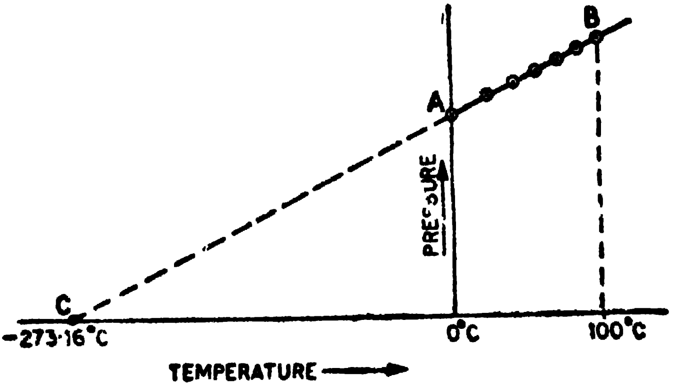


Fig. 2·20

straight line (Fig. 2·20). If the graph is extrapolated, it will meet the X axis at $-273{\cdot}16$°C and this temperature is called absolute zero.

The value of the pressure coefficient is

$$= \frac{1}{273{\cdot}16} = 0{\cdot}0036608 \text{ per °C}$$

If P_1 and P_2 are the pressures of a given mass of gas at temperatures t_1°C and t_2°C and if P_0 is the pressure at 0°C

$$P_1 = P_0[1+\gamma_p t_1]$$

$$P_2 = P_0[1+\gamma_p t_2]$$

$$\frac{P_2}{P_1} = \frac{1+\gamma_p t_2}{1+\gamma_p t_1}$$

or

$$\gamma_p = \frac{P_2-P_1}{P_1t_2-P_2t_1}$$

Using this [illegible] γ_p can be calculated for different ranges of temperature

The value of γ_p can also be calculated by finding the absolute zero from the graph. The reciprocal of this temperature measures γ_p. If the value of absolute zero is $-273{\cdot}16$°C, then

$$\gamma_p = \frac{1}{273{\cdot}16}$$

2·28 Determination of the Volume Coefficient of a Gas

The volume coefficient of a gas can be determined in the laboratory by the following method. The apparatus consists of a glass bulb *B* connected to a reservoir *R* containing mercury. The bulb *B* is surrounded by the outer glass jacket through which steam can be passed. A thermometer is fixed to note the temperature.

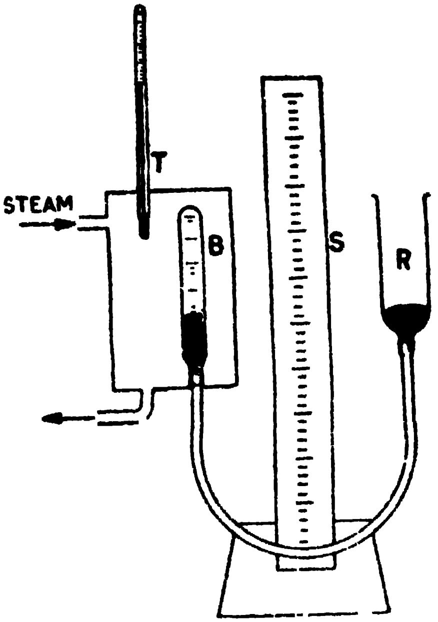


Fig. 2·21

Initially water at 0°C is circulated through the jacket and the reservoir *R* is adjusted so that the level of Hg in *B* and *R* is the same. It means that the pressure of air in the bulb *B* is equal to the atmospheric pressure. Let the volume of the gas in the bulb *B* at 0°C be V_0.

Now, steam is passed through the jacket and when the temperature is constant as indicated by the thermometer, the levels of Hg in *B* and *R* are adjusted to be the same. It means the pressure of the gas in the bulb *B* is again equal to the atmospheric pressure. Let the volume of the gas at t°C be V_t.

Then $$\gamma_v = \frac{V_t - V_0}{V \times t} \ /°C$$

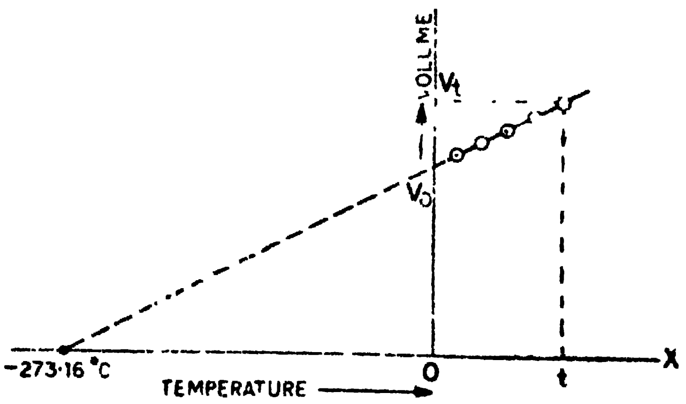


Fig. 2·22

The volume coefficient calculated is about

$$\frac{1}{273\cdot16} = 0\cdot0036608 \ /°C$$

To plot a graph between the volume and temperature, a large number of readings are obtained after the steam is cut off. A graph *is drawn between temperature along the X-axis and the volume along the Y-axis. The graph is a straight line. If the graph is extrapolated* it meets the X-axis at $-273{\cdot}16$°C. This corresponds to absolute zero. Also, the reciprocal of this temperature measures the volume coefficient, *i.e.*,

$$\gamma_v = \frac{1}{273{\cdot}16}$$

$$= 0{\cdot}0036608/°\text{C}$$

It is found that the volume coefficient of a gas is equal to the pressure coefficient provided the gas obeys the Boyle's law and the Charles' law.

Gas	*Pressure coefficient* γ_p	*Volume coefficient* γ_v
Hydrogen	0·0036610	0·0036611
Helium	0·0036609	0·0036607
Nitrogen	0·0036606	0·0036609

Exercises II

1. Define coefficient of linear expansion, cubical expansion and superficial expansion. Derive the relation between them.

2. Describe Fizeau's method for determining the coefficient of linear expansion of a crystal. Discuss Tutton's modification.

3. Describe how the coefficient of linear expansion of a solid can be determined with the help of an interference method.

(*Agra 1966*)

4. Describe an experiment to determine the coefficient of cubical expansion of mercury.

5. Describe an experiment to find the volume coefficient of a gas.

6. Describe an experiment to find the pressure coefficient of a gas. Are the volume and pressure coefficient of a gas equal ?

7 A steel beam of length 6 metres is fixed rigidly between two supports Calculate the stress in the rod for an increase in temperature of 20°C

($\alpha = 12\times10^{-6}$/°C and $Y = 2\times10^{12}$ dynes/sq cm)

[**Ans.** 480×10^{6} dynes]

8. A steel wire 10 metres long and 2 mm in diameter is fixed between two rigid supports. Calculate the increase in tension when the temperature falls through 30°C.

($\alpha = 12\times10^{-6}$/°C and $Y = 2\times10^{12}$ dynes/sq cm)

[**Ans.** $22{\cdot}627\times10^{6}$ dynes]

9. A uniform rod 4 sq mm in cross-section is heated from 0°C to 40°C. Find the force which must be exerted to prevent it from expanding. Find the energy stored per unit volume.

($\alpha = 12 \times 10^{-6}$/°C and $Y = 10^{11}$ newtons/sq m)

[**Ans.** Force = 192 newtons, Energy per unit volume = 11,520 joules/cubic metre]

10. A steel wire of diameter 2 mm supports a load which is sufficient to keep the wire taut at 50°C. Calculate the additional load that will be required to restore the length of the wire to its initial value when the temperature falls to 40°C.

[**Ans.** 7·694 kg wt]

11. Write short notes on :

(*a*) Expansion of crystals

(*b*) Anomalous expansion of water.

(*c*) Dulong and Petit's method.

(*d*) Thermal stress in beams due to expansion.

(*e*) Callendar and Moss experiment.

(*f*) Optical lever method for determining α.

12. In Tutton's experiment for determining the coefficient of expansion of a crystal, the following data were observed. Thickness of the crystal = 5 mm, wavelength of light used $= 5{,}890 \times 10^{-8}$ cm. When the temperature of the crystal was increased from 25°C to 55°C, the number of fringes that crossed the field of view was found to be 7. Calculate the coefficient of linear expansion of the crystal.

[**Ans.** $13 \cdot 74 \times 10^{-6}$/°C]

3

Calorimetry

3·1 Definitions

When a body is heated, its temperature rises. If 100 g of copper and 100 g of water are heated by similar burners for the same time, the rise in temperature is not the same in the two cases. The rise in temperature depends on the quantity of heat given to the body and the nature of its material. Let H be the quantity of heat given to a body of mass m and let the rise in temperature be θ.

Then, $$H = mC\theta$$

where C is a constant that depends upon the nature of the substance. C is called the specific heat of the substance.

Calorie. It is the quantity of heat required to raise the temperature of one gram of water from 14·5°C to 15·5°C. This is the standard unit recommended by International Committee of Pure Physics.

For ordinary purposes, the specific heat of water is taken as 1 but specific heat of water is not 1 at all temperatures. For practical purposes *Calorie* may be defined as the amount of heat required to raise the temperature of 1 gram of water through 1°C.

Kilogram Calorie It is the amount of heat required to raise the temperature of 1 kg of water through 1°C.

$$1 \text{ kg calorie} = 1000 \text{ calories} = 1 \text{ kilocalorie}$$

British Thermal Unit. It is the amount of heat required to raise the temperature of 1 pound of water through 1°F.

$$1\ B.T.U. = 252 \text{ calories}$$

Therm. It is the amount of heat required to raise the temperature of 10^5 pounds of water through 1°F.

$$1 \text{ Therm} = 2{\cdot}52 \times 10^7 \text{ calories}$$

Pound Calorie. It is the amount of heat required to raise the temperature of 1 pound of water through 1°C.

$$1 \text{ pound calorie} = 453{\cdot}6 \text{ calories}$$

It is called centigrade heat unit.

Units of Heat

Unit	*Quantity of water*	*Rise in temp.*	*Relation*
Calorie	1 g	1°C	= 1 Calorie
Kg Calorie	1 kg	1°C	= 1000 Calories
BTU	1 pound	1°F	= 252 ,,
Therm	10^5 pounds	1°F	= 2.52×10^7 ,,
Pound Calorie	1 pound	1°C	= 453.6 ,,

Specific Heat. It is defined as the quantity of heat required to raise the temperature of unit mass of a substance through one degree.

Suppose,

Mass of the substance = m

Sp. heat of the substance = C

Rise in temperature = θ

$$H = mC\theta$$

or

$$C = \frac{H}{m\theta}$$

Unit of specific heat. In C.G.S. system, the unit of H is in calories, m is in grams and θ is in °C. Therefore the unit of specific heat will be

$$C = \frac{\text{calorie}}{g\ °C}$$

$$= \text{calorie/g °C}$$

The specific heat of a substance is not constant and it is different at different temperatures. Ordinarily, the specific heat determined is the mean specific heat. Suppose m is the mass of the substance, C the mean specific heat and H units of heat is required to raise its temperature from θ_1 to θ_2, then the mean specific heat

$$C = \frac{H}{m(\theta_2 - \theta_1)}$$

For qualitative work if dQ heat is given to raise the temperature of m g of a substance through $d\theta$,

$$dH = m\,C\,d\theta$$

$$C = \frac{1}{m}\,\frac{dH}{d\theta}$$

Thermal Capacity. It is the quantity of heat required to raise the temperature of the whole of the substance through 1°C. Let the mass of the substance be m and its specific heat C.

Thermal capacity $= m \times C \times 1$

$= m\,C$ calories/°C

Water Equivalent. It is the amount of water that will absorb the same quantity of heat as the substance for the same rise in temperature. Let the mass of the substance be m, specific heat C and rise in temperature θ.

$$H = m\,C\,\theta$$

If the water equivalent $= w$

$$H = w \times 1 \times \theta$$

$$\therefore \quad w \times 1 \times \theta = m\,C\,\theta$$

or $$w = m\,C \text{ grams}$$

Water equivalent is numerically equal to the thermal capacity but the unit of water equivalent is grams and that of thermal capacity is calories.

3.2 Regnault's Method of Mixtures

Specific heat of solids Regnault was the first to devise the apparatus commonly used in the laboratories to find the specific heat of a solid or liquid employing the method of mixtures In this the given solid is heated to a constant high temperature and then it is quickly transferred into a calorimeter containing water at room temperature The final temperature of the mixture is noted. From the principle that heat lost by the solid is equal to the heat gained by the calorimeter and contents, the specific heat of the given solid is calculated

3.3 Copper Block Calorimeter

Specific heat of a solid at high temperature cannot be determined by ordinary apparatus used in the laboratory. Steam or vapours produced would cause considerable loss of heat when a hot solid is mixed with water or a liquid The result obtained will not be accurate To overcome this difficulty, *Nernst* and *Lindemann* designed a calorimeter called the *copper block calorimeter*

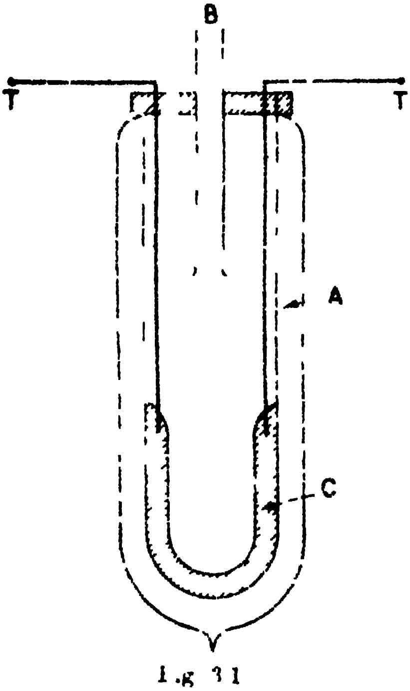


Fig 3 1

It consists of a Dewar flask A having a copper block C fixed inside it. T, T are the terminals of the leads of the thermocouple to measure the temperature of the block C The flask is covered from outside to prevent any loss of heat to the surroundings Through the tube B, a hot solid can be dropped (Fig 3 1)

The substance whose specific heat is to be determined is heated to a known high temperature and then gently dropped through the tube B into the block C The copper block has high thermal conductivity and a uniform final temperature is reached in a short time The temperature is measured with the help of a calibrated thermocouple, the copper block C [illegible] as the hot end. To avoid air currents the tube B is closed with an automatic electrical arrangement after the substance has been dropped into the block C. The whole apparatus can be maintained at a desired temperature. From the heat gained by copper block and the heat lost by the substance, the specific heat of the substance can be calculated.

Magnus determined the specific heat of platinum and other metals up to 900 C. Jaeger and his co-workers determined the specific heat of Pt, tungsten, Rh, Ir and other metals up to 1600 C. In order to find the specific heat at high temperatures, say, between 700 C and 800 C the experiment is performed twice, first at 700°C and then at 800 C. The mean value of the specific heat is calculated.

3 4 Nernst Vacuum Calorimeter

This calorimeter is used to find the specific heat of solids at low temperature. Nernst and Lindemann performed a number of accurate experiments to determine the specific heat of solids at low temperatures.

The Nernst calorimeter consists of an evacuated flask D in which the metal whose specific heat is to be determined, is suspended as shown in Fig 3 2. P and Q are two non conducting loops. The cylinder B and the cylindrical plug A are made of the same metal. The heating coil C is made of platinum and is wound around A. The leads LL are connected to an electrical heating arrangement. The cylinder A fits completely inside the cylinder B. The heating coil C also serves as a platinum resistance theromometer to measure the temperature of the metal.

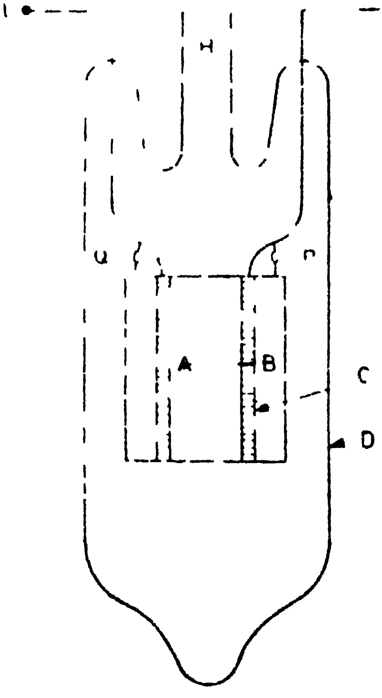


Fig. 3 2

Suppose the resistance of the platinum wire is R_1 at temperature θ_1. R_1 is found by measuring the current in the wire and the potential difference across the two ends of the wire. Let the potential difference be E and the current I_1.

$$\therefore R_1 = \frac{E}{I_1} \quad \text{(At temperature } \theta_1\text{)}$$

Similarly resistance R_2 at temperature θ_2 is given by

$$R_2 = \frac{E}{I_2} \quad \text{(At temperature } \theta_2\text{)}$$

The platinum wire is initially calibrated and from these values corresponding to R_1 and R_2 the values θ_1 and θ_1 are found.

The flask D is kept in a bath containing ice, liquid air etc., depending upon the low temperature at which the specific heat of the given metal is to be determined. After the flask D has attained the temperature of the bath, it is evacuated. *This initial temperature of the metal is found. Let it be θ_1. Electric current is passed through the coil C for a known time so that the rise in temperature is about* 1°C. Suppose the final temperature of the metal is θ_2.

Mass of the metal $= M$ grams

Specific heat $= C$

Rise in temperature $= (\theta_2 - \theta_1)$

Voltmeter reading $= E$ volts

Ammeter reading $= I$ amperes

Time for which current is passed $= t$ seconds

$$\therefore \quad MC(\theta_2 - \theta_1) = \frac{EIt}{4{\cdot}2}$$

$$C = \frac{EIt}{4{\cdot}2\, M(\theta_2 - \theta_1)}$$

In this experiment, the heat losses are practically eliminated as the experiment is performed in vacuum. However, a correction is required for the little loss of heat due to radiation.

To determine the specific heat of non-metals, the substance is kept inside a silver vessel. The heating coil is wound round the silver vessel. The experiment is performed in vacuume by suspending the silver vessel inside the flask D.

Specific Heats and Atomic Heats of Solids at 20 °C

Element	*Specific Heat*	*Atomic Heat*
Aluminium	0·212	5·72
Boron	0·307	3·32
Carbon	0·160	1·92
Copper	0·091	5·79
Gold	0·031	6·11
Iron	0·110	6·12
Lead	0·030	6·21
Silicon	0·182	5·11
Silver	0·056	6·04
Tin	0·054	6·31

3·5 Newton's Law of Cooling

Newton's Law of Cooling states that the rate of loss of heat of a body is directly proportional to the *difference of temperature of* the body and the surroundings. *The law holds good only for small* difference of temperature. Also, the loss of heat by radiation depends upon the nature of the surface of the body and the area of the exposed surface.

$$\frac{dH}{dt} \propto (\theta-\theta_0) \quad \text{or} \quad -\frac{dH}{dt} = k\,(\theta-\theta_0)$$

Consider a body of mass m, specific heat C and at temperature θ. Let θ_0 be the temperature of the surroundings. Suppose, the temperature falls by a small amount $d\theta$ in time dt. Then the amount of heat lost

$$dH = mCd\theta$$

∴ Rate of loss of heat

$$\frac{dH}{dt} = mC\,\frac{d\theta}{dt} \qquad \ldots(i)$$

From Newton's law of cooling

$$-\frac{dH}{dt} = k\,(\theta-\theta_0) \qquad \ldots(ii)$$

where k is a constant depending upon the area and the nature of the surface of the body.

From (i) and (ii)

$$-mC\frac{d\theta}{dt} = k(\theta-\theta_0)$$

or

$$\frac{d\theta}{\theta-\theta_0} = -\frac{k}{mC}\,.\,dt = -K.dt \qquad \ldots(iii)$$

Integrating,

$$\log\,(\theta-\theta_0) = -Kt+c \qquad \ldots(iv)$$

If a graph is plotted between t along the X-axis and $\log\,(\theta-\theta_0)$ along the Y-axis, it is a straight line. Hot water is taken in a

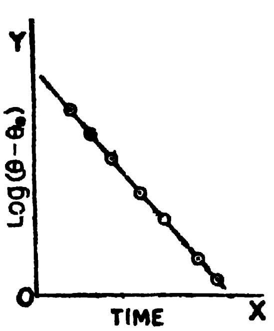


Fig. 3·3 (i)

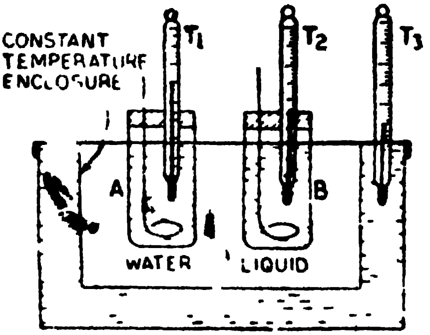


Fig. 3·3 (ii)

calorimeter and is placed in a double walled vessel. Temperature of water after regular intervals of time is noted. A graph between log $(\theta-\theta_0)$ and time t is plotted [Fig 3 3 (i)]. It is a straight line. This verifies Newton's law of cooling

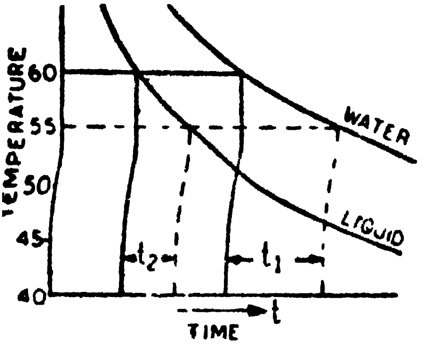


Fig 3 4

Fig 3 4

Specific heat of a liquid. *A and B are two identical calorimeters containing equal volumes* of hot water and the hot liquid respectively. The two calorimeters are made of the same material and their outer surfaces are equally polished. The calorimeters are kept inside a constant temperature enclosure. The thermometers T_1 and T_2 measure the temperature of water and liquid [Fig 3 3 (ii)]. The temperature of the two calorimeters are noted after regular intervals of time (say one minute). Graphs are plotted between temperature and time, for water and the liquid (Fig 3 4).

From equation (iii)

$$\int \frac{d\theta}{\theta-\theta_0} = -\frac{k}{mC}\int dt$$

In the case of water, suppose

Mass of water = m

Water equivalent of the calorimeter $A = w$

Time taken by water to cool from 60°C to 55°C = t_1

$$\therefore \int_{60}^{55} \frac{d\theta}{\theta-\theta_0} = -\frac{k}{(m+w)}\, t_1 \qquad \ldots(v)$$

Suppose mass of the liquid = M

Water equivalent of the calorimeter $B = w$

Specific heat of the liquid = C

Time taken by the liquid to cool from 60°C to 55°C = t_2

$$\therefore \int_{60}^{55} \frac{d\theta}{\theta-\theta_0} = -\frac{k}{(MC+w)}\, t_2 \qquad \ldots(vi)$$

From equations (v) and (vi)

$$\frac{MC+w}{t_2} = \frac{(m+w)}{t_1}$$

or

$$C = \frac{(m+w)t_2}{Mt_1} - \frac{w}{M} \qquad \ldots(vii)$$

Example 3 1. *A liquid takes 5 minutes to cool from 80°C to 50°C. How much time will it take to cool from 60°C to 30°C ? The temperature of the surrounding is 20°C* (*Punjab 1964*)

$$\int \frac{d\theta}{\theta-\theta_0} = -K\int dt$$

$$\theta_0 = 20\ °C$$

In the first case,

$$\int_{80}^{50} \frac{d\theta}{\theta-\theta_0} = -K\times 5$$

$$\log\left[\theta-\theta_0\right]_{80}^{50} = 5K$$

$$\log\left(\frac{50-20}{80-20}\right) = -5K$$

$$\log\frac{30}{60} = -5K$$

or

$$\log\frac{60}{30} = 5K$$

In the second case, suppose the time taken is t minutes,

$$\int_{60}^{30}\frac{\theta}{\theta-\theta_0} = -K \qquad \ldots(i)$$

$$\log\left(\frac{30-20}{60-20}\right) = -Kt$$

$$\log\frac{10}{40} = -Kt$$

or

$$\log\frac{40}{10} = -Kt \qquad \ldots(ii)$$

Dividing (ii) by (i)

$$\frac{t}{5} = \frac{\log 4}{\log 2} = 2$$

$$t = \mathbf{10\ minutes}$$

Example 3·2. *Equal volumes of water (density 1* g/cm³*) and alcohol (density 0·8* g/cm³*) when put in similar calorimeters take 100 seconds and 74 seconds respectively to cool from 50 °C to 40 °C. Calculate the specific heat of alcohol. Thermal capacity of each calorimeter is numerically equal to the volume of either liquid.*

(Punjab 1966)

Let the volume of either liquid be V

Mass of water $= m = V\times 1$

Mass of alcohol $= M\times V\times 0{\cdot}8$

Water equivalent of each calorimeter $= w = V$

Here $t_1 = 100$ s, $t_2 = 74$ s

$$\frac{MC+w}{t_2} = \frac{m+w}{t_1}$$

$$C = \frac{(m+w)\,t_2}{Mt_1} - \frac{w}{M}$$

$$= \frac{(V+V)\,74}{V\times 0{\cdot}8\times 100} - \frac{V}{V\times 0{\cdot}8}$$

$$C = \mathbf{0{\cdot}6\ calorie/g-K}$$

Example 3·3. *A body cools in 5 minutes from 60°C to 40°C. What will be its temperature after the next 5 minutes ? Temperature of the surroundings = 10°C. Assume that the Newton's law of cooling holds good throughout the process.*

$$\int_{\theta_1}^{\theta_2} \frac{d\theta}{\theta-\theta_0} = -K\int dt = -Kt$$

(1) In the first case, $\theta_0 = 10°\text{C}$,

$$\theta_1 = 60°\text{C},\ \theta_2 = 40°\text{C},\ t = 5 \text{ minutes}$$

$$\int_{60}^{40} \frac{d\theta}{\theta-\theta_0} = -5K$$

$$\Big[\log(\theta-\theta_0)\Big]_{60}^{40} = -5K$$

$$\log\left(\frac{40-10}{60-10}\right) = -5K \qquad \ldots(i)$$

(2) In the second case

$$\theta_0 = 10°\text{C},$$

$$\theta_1 = 40°\text{C},\ \theta_2 = x,\ t = 5 \text{ minutes}$$

$$\int_{40}^{x} \frac{d\theta}{\theta-\theta_0} = -5K$$

$$\log\left(\frac{x-10}{40-10}\right) = -5K \qquad \ldots(ii)$$

From equations (*i*) and (*ii*)

$$\log\left(\frac{x-10}{40-10}\right) = \log\left(\frac{40-10}{60-10}\right)$$

$$\frac{x-10}{30} = \frac{30}{50}$$

$$x = 28°\text{C}$$

Example 3·4 *A liquid takes 4 minutes to cool from 70°C to 50 °C How much time will it take to cool from 50 °C to 40 °C ? The temperature of the surroundings is 25 °C. Newton's law of cooling is applicable throughout the process.*

$$\int_{\theta_1}^{\theta_2} \frac{d\theta}{\theta-\theta_0} = -K\int dt = -Kt$$

(1) In the first case,

$$\theta_0 = 25\ °\text{C},$$

$$\theta_1 = 70\ °\text{C},\ \theta_2 = 50\ °\text{C},\ t = 4 \text{ minutes}$$

$$\int_{70}^{50} \frac{d\theta}{\theta-\theta_0} = -4K$$

$$\log_e\left(\frac{50-25}{70-25}\right) = -4K \qquad \ldots(i)$$

(2) In the second case

$$\theta_0 = 25°\text{C},$$

$$\theta_1 = 50°\text{C},\ \theta_2 = 40°\text{C},\ t = ?$$

$$\int_{50}^{40} \frac{d\theta}{\theta-\theta_0} = -Kt$$

$$\log_e \left(\frac{40-25}{50-25}\right) = -Kt \qquad \ldots(ii)$$

Dividing (*ii*) by (*i*)

$$\frac{t}{4} = \frac{\log_e\left(\frac{15}{25}\right)}{\log_e\left(\frac{25}{45}\right)}$$

$$t = \frac{4\times 2\cdot3026}{2\cdot3026}\left[\frac{\log_{10}(0\cdot6)}{\log_{10}(0\cdot55)}\right]$$

$$= 4\left[\frac{\log_{10}(0\cdot6)}{\log_{10}(0\cdot55)}\right]$$

$$= 4\left[\frac{\bar{1}\cdot7782}{\bar{1}\cdot7404}\right] = 4\left[\frac{-0\cdot2218}{-0\cdot2596}\right]$$

$$= \frac{8872}{2596}$$

$$= \mathbf{3\cdot418\ min.}$$

Example 3·5. *A liquid cools in 6* minutes *from 80 °C to 60 °C. What will be its temperature after the next 10* minutes *? Temperature of the surroundings is 30 °C. Assume that the Newton's law of cooling is applicable throughout the process.*

$$\int_{\theta_1}^{\theta_2} \frac{d\theta}{\theta-\theta_0} = -K\int dt = -Kt$$

(1) In the first case,

$$\theta_0 = 30°\text{C},$$

$$\theta_1 = 80°\text{C},\ \theta_2 = 60°\text{ C},\ t = 6\text{ min}$$

$$\int_{80}^{60} \frac{d\theta}{\theta-\theta_0} = -6K$$

$$\log\left(\frac{60-30}{80-30}\right) = -6K$$

$$\log 0\cdot6 = -6K \qquad \ldots(i)$$

(2) In the second case,

$$\theta_0 = 30\ °\text{C},$$

$$\theta_1 = 60\ °\text{C},\ \theta_2 = x,\ t = 10\text{ min.}$$

$$\int_{60}^{x} \frac{d\theta}{\theta-\theta_0} = -10K$$

$$\log\left(\frac{x-30}{60-30}\right) = -10K$$

Dividing (*ii*) by (*i*)

$$\frac{\log\left(\frac{x-30}{60-30}\right)}{\log(0{\cdot}6)} = \frac{10}{6}$$

$$\log\left(\frac{x-30}{60-30}\right) = \frac{5}{3}\log(0{\cdot}6)$$

$$\log\left(\frac{x-30}{30}\right) = \log(0{\cdot}6)^{5/3}$$

$$\frac{x-30}{30} = (0{\cdot}6)^{5/3}$$

$$\mathbf{x = 42{\cdot}80\ ^\circ C}$$

Example 3·6. *A body initially at 80 °C cools to 64 °C in 5* minutes *and to 52 °C in 10* minutes. *What will be its temperature after 15* minutes *and what is the temperature of the surroundings ?*

[*Delhi (Additional Physics) 1975*]

$$\int_{\theta_1}^{\theta_2}\frac{d\theta}{\theta-\theta_0} = -K\int dt = -Kt$$

(1) In the first case

$$\theta_1 = 80^\circ C,\ \theta_2 = 64^\circ C,\ t = 5 \text{ min}$$

$$\int_{80}^{64}\frac{d\theta}{\theta-\theta_0} = -5K$$

$$\log\left(\frac{64-\theta_0}{80-\theta_0}\right) = -5K \qquad \ldots(i)$$

(2) In the second case,

$$\theta_1 = 64^\circ C,\ \theta_2 = 52^\circ C,$$

$$t = 10-5 = 5 \text{ min}$$

$$\int_{64}^{52}\frac{d\theta}{\theta-\theta_0} = -5K$$

$$\log\left(\frac{52-\theta_0}{64-\theta_0}\right) = -5K \qquad \ldots(ii)$$

From equations (*i*) and (*ii*)

$$\frac{64-\theta_0}{80-\theta_0} = \frac{52-\theta_0}{64-\theta_0}$$

$$\therefore \qquad \mathbf{\theta_0 = 16^\circ C}$$

(*iii*) Let the temperature after 15 minutes be θ_2

$$\theta_1 = 52^\circ C,\ \theta_0 = 16^\circ C,$$

$$t = 15-10 = 5 \text{ minutes}$$

$$\int_{52}^{\theta_2} \frac{d\theta}{\theta-\theta_0} = -5K$$

$$\log\left(\frac{\theta_2-16}{52-16}\right) = -5K \qquad \ldots(iii)$$

Equating (*ii*) and (*iii*)

$$\frac{\theta_2 - 16}{52-16} = \frac{52-16}{61-16}$$

$$\theta_2 = 43°C$$

Example 3.7. *Find the specific heat of a liquid which takes 2 minutes in cooling from 50°C to 40°C in a vessel in which the same volume of water takes 5 minutes in cooling through the same range of temperature. Mass of water = 100 g, mass of liquid = 85 g, water equivalent of the vessel = 10 g.*

[*Delhi*, 1976]

$$\frac{MC+w}{t_2} = \frac{m+w}{t_1}$$

Here

$M = 85$ g

$C = ?$

$w = 10$ g

$m = 100$ g

$t_2 = 2$ minutes $= 120$ s

$t_1 = 5$ minutes $= 300$ s

$$C = \left[\frac{(m+w)\,t_2}{Mt_1}\right] - \frac{w}{M}$$

$$C = \left[\frac{(100+10)\,120}{85\times300}\right] - \frac{10}{85}$$

$C = 0\cdot4$ calories/g-K

3.6 Specific Heat of a Liquid - Joule's Electrical Method

The apparatus consists of a calorimeter in which a heater coil (wire) of resistance *R* is enclosed. The two ends of the wire are connected to the terminals on the lid. The calorimeter is enclosed in a wooden box. The wire *R* is connected in series with a battery, a key, a rheostat and an ammeter. A voltmeter is connected parallel to the wire (Fig. 3·5).

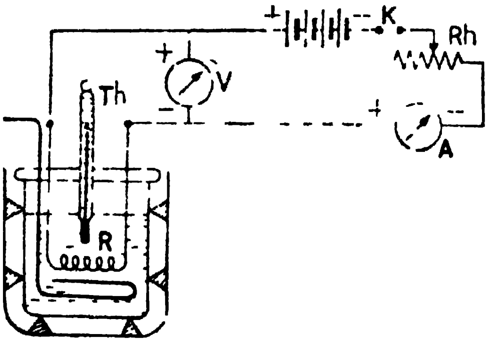


Fig. 3·5.

The liquid whose specific heat is to be determined is taken in the calorimeter. Current is passed through the wire for a known interval of time. The rise in temperature of the calorimeter and the liquid is noted with the help of a thermometer. The current is passed for such a time that the rise in temperature is about 10°C.

Suppose, the mass of the liquid is M, specific heat of the liquid is C and water equivalent of the calorimeter is w.

Initial temperature of the liquid $= \theta_1$°C

Final temperature of the liquid $= \theta_2$°C

P.D. across the wire $= E$ volts

Current flowing $= I$ amperes

Time $= t$ seconds

Heat produced $= \frac{E.I.t}{4{\cdot}2}$ calories

Heat gained by the liquid and the calorimeter

$$= (MC+w)\,(\theta_2-\theta_1)$$

$$\therefore\ (MC+w)(\theta_2-\theta_1) = \frac{E.I.t}{4{\cdot}2}$$

$$C = \frac{E.I.t}{4{\cdot}2\,(\theta_2-\theta_1)\,M} - \frac{w}{M}$$

3·7 Specific Heat of a Liquid—Callendar and Barnes' Continuous Flow Method

The apparatus consists of a glass tube in which a resistance wire is enclosed. The ends of the wire are connected to the terminals outside the tube. Thermometers T_1 and T_2 measure the temperature of the incoming and outgoing liquid. The liquid is passed through the tube at a uniform rate. The electrical connections are made as shown in Fig. 3·6. A vacuum jacket surrounding the glass tube is provided to avoid loss of heat by conduction and convection. Current and the rate of flow of water are adjusted so that the thermometers how a difference of about 10°C.

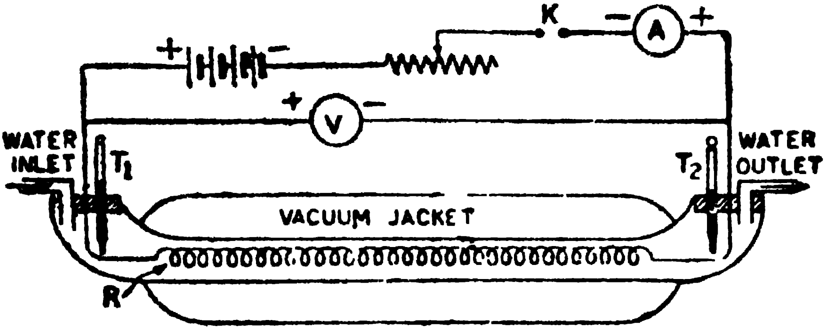


Fig. 3·6

Let, E, I and t be the potential difference, current and time for which the liquid is collected. If the mass of liquid collected is m and the difference of temperature between the two thermometers is $(\theta_2 - \theta_1)$, then

$$mC\ (\theta_2 - \theta_1) + R = \frac{E.I.t.}{4{\cdot}2} \qquad ...(i)$$

where R is the loss of heat by radiation. The current through the wire is changed The rate of flow is adjusted so that the difference of temperature $(\theta_2 - \theta_1)$ remains the same. Suppose the amount of liquid collected in time t is m'

$$\therefore \quad m'C(\theta_2 - \theta_1) + R = \frac{E'I't}{4{\cdot}2} \qquad ...(ii)$$

Subtracting (ii) from (i)

$$(m - m')C(\theta_2 - \theta_1) = \frac{(EI - E'I')\,t}{4{\cdot}2}$$

$$C = \frac{(EI - E'I')\,t}{4{\cdot}2\,(m - m')(\theta_2 - \theta_1)}$$

This is an accurate method because the observations are taken under steady state. The thermal capacity of the apparatus does not occur in the calculation. Moreover, the errors due to loss of heat by conduction, convection and radiation have been practically eliminated

3 8 Experimental Determination of Heat Capacities

In modern methods, measurement of heat capacity of substances involves the supply of heat to the system from an electrical source. From the energy received from the source in a given interval of time, a part of it may be used in raising the temperature of the system and the remainder is lost to the surroundings at a lower temperature (Fig. 3·7).

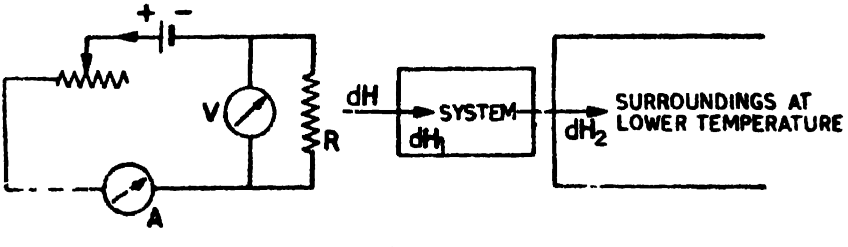


Fig. 3·7

Let dH be the quantity of heat drawn from the electrical source in time dt. Here dH_1 is the amount of heat retained by the system to raise its temperature by $d\theta$ and dH_2 is the amount of heat lost to the surroundings.

$$dH = dH_1 + dH_2$$

$$dH_1 = 1 \times C_p \times dT$$

Here C_p is the specific heat of a substance at constant pressure. If the potential difference across the heater wire is E volts and the current flowing is I amperes, then

$$dH = \frac{EI.dt}{J}$$

$$\therefore \quad dH_1 = dH - dH_2$$

$$C_p \times dT = \frac{EI\,dt}{J} - dH_2 \qquad \ldots(i)$$

If the system does not lose heat to the surroundings, then

$$dH_2 = 0$$

$$\therefore \quad C_p \times dT = \frac{EI\,dt}{J} \qquad \ldots(ii)$$

$$\frac{EI}{J} = C_p\left[\frac{dT}{dt}\right] \qquad \ldots(iii)$$

To find $\frac{dT}{dt}$, *i.e.*, the rate of rise of temperature of the system with time, a curve is drawn between temperature (T) and time (t). From the graph $\frac{dT}{dt}$ is found for the temperature at which C_p is to be determined.

3·9. Adiabatic Vacuum Calorimeter

This calorimeter was designed by Nernst and later on modified by Simon and Lange. Inside a thin copper vessel C, the substance is taken. The vessel C also contains heating coils and a sensitive platinum resistance thermometer to note the temperature. A thermostat B is made of copper and surrounds the vessel C. It is also heated electrically. The two junctions of the sensitive thermocouple are in contact with the inner surface of B and the outer surface of C.

The outer vessel A is surrounded by liquid hydrogen contained in a vacuum flask. The current through the heater coil of B is adjusted so that the thermocouple shows no deflection. This ensures a uniform temperature enclosure for C.

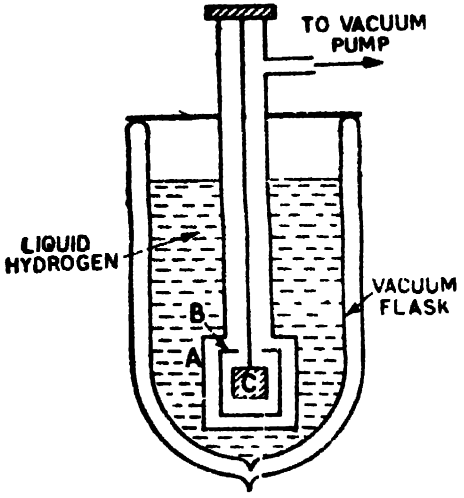


Fig. 3·8

The space inside A is evacuated with the help of a vacuum pump. If the rise in temperature of 1 gram of the substance is dT in time dt,

Then $$\frac{EI}{J} = C_p\left[\frac{dT}{dt}\right] \qquad ...(iv)$$

The method is useful in determining the heat capacity of substances at low temperatures.

To find the value of C_v, it is difficult to find its value experimentally at low temperature. Its value is calculated from the equation

$$C_v = C_p - \frac{r}{J} \qquad ...(v)$$

3·10 Two Specific Heats of a Gas

Consider a gas of mass m at a pressure P and volume V. If the gas is compressed, there is rise in temperature. In this case, no heat has been supplied to the gas to raise its temperature.

$\therefore$ Specific heat, $C = \dfrac{H}{m\theta}$

But $H = 0$

$\therefore$ $C = 0$

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

$$C = \frac{H}{m\theta}$$

Here $\theta = 0$

$\therefore$ $C = \dfrac{H}{m \times 0} = \infty$

Thus, the specific heat of a gas varies from zero to infinity.

In order to fix the value of the specific heat of a gas, the pressure or volume has to be kept constant. Consequently, a gas has two specific heats.

(1) Specific heat at constant volume C_v,

(2) Specific heat at constant pressure C_p.

C_v. It is defined as the quantity of heat required to raise the temperature of one gram of a gas through 1°C at constant volume.

C_p. It is defined as the quantity of heat required to raise the temperature of one gram of a gas through 1°C at constant pressure.

C_p is greater than C_v. When a gas is heated at constant volume, the heat supplied to the gas is wholly used up to raise its temperature. On the other hand when a gas is heated at constant pressure, a part of the heat is used to raise its temperature and a part is used to do external work to keep the pressure constant.

$$C_p > C_v$$

Relation. Consider one gram of a gas at a pressure P, volume V and temperature T. Heat is supplied to the gas to raise its temperature through dT. As the pressure has to remain constant,

$$\text{Work done, } W = P \times A \times x = P \times dV$$

where dV is the change in volume.

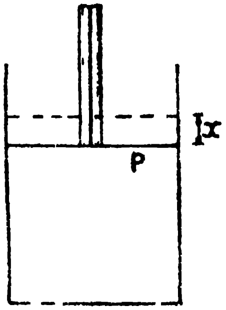


Fig. 3·9

From the gas equation

$$PV = rT,$$

Differentiating,

$$PdV + VdP = r\,dT$$

But $\qquad dP = 0$

$$\therefore \quad PdV = rdT$$

$\therefore$ Work done in heat units

$$= \frac{r.dT}{J} \text{ calories}$$

Heat supplied $\qquad = 1 \times C_p \times dT$

$$= 1 \times C_v \times dT + \frac{r \cdot dT}{J}$$

or $\qquad C_p - C_v = \frac{r}{J}$

where r is the gas constant for one gram of a gas If C_p and C_v represent gram molecular specific heats, then

$$C_p - C_v = \frac{R}{J}$$

where R is the universal gas constant.

Example 3 8. *Find the value of the universal gas constant R for one gram molecule of a gas.*

One gram molecule of a gas at N T.P. occupies 22400 cm^3

$$P = 76 \text{ cm of Hg} = 76 \times 13{\cdot}6 \times 981 \text{ dynes/cm}^2$$

$$V = 22400 \text{ cm}^3$$

$$T = 273 \text{ K}$$

$$PV = RT$$

or $$R = \frac{PV}{T} = \frac{76 \times 13{\cdot}6 \times 981 \times 22400}{273}$$

$$\mathbf{R = 8{\cdot}31 \times 10^7 \text{ ergs/mole-K}}$$

Note. The value of R is the same for all gases, provided the mass of the gas is one gram molecule.

Example 3·9. *Calculate the specific heat of air at constant volume, given that specific heat at constant pressure is 0·23, density of air at* N.T.P. *1·293* gram/litre *and* $J = 4{\cdot}2 \times 10^7$ ergs/cal.

(Punjab 1966)

$$C_p = 0{\cdot}23,\ J = 4{\cdot}2 \times 10^7 \text{ ergs/cal},\ C_v = ?$$

Density of air at N.T.P. $= 1{\cdot}293$ g/litre

Volume of one gram of air at N.T.P.

$$= \frac{1000}{1{\cdot}293} \text{ cc}$$

$$PV = rT$$

$$r = \frac{PV}{T}$$

$$= \frac{76 \times 13{\cdot}6 \times 980 \times 1000}{273 \times 1{\cdot}293}$$

$$C_p - C_v = \frac{r}{J}$$

$$C_v = C_p - \frac{r}{J}$$

$$= 0{\cdot}23 - \frac{76 \times 13{\cdot}6 \times 980 \times 1000}{273 \times 1{\cdot}293 \times 4{\cdot}2 \times 10^7}$$

$$C_v = 0{\cdot}23 - 0{\cdot}0683$$

$$= \mathbf{0{\cdot}1617}$$

Example 3·10. *Calculate the difference in the two specific heats of one gram of helium, given that the molecular weight of helium = 4 and the gram molecular volume of helium at* N.T.P. = *22·4* **litres.**

(Delhi 1975)

$$C_p - C_v = \frac{r}{J}$$

Volume of one gram of helium at N.T.P.

$$V = \frac{22400}{4} = 5600 \text{ cm}^3$$

$$PV = rT$$

$$r = \frac{PV}{T}$$

or

$$r = \frac{76 \times 13 \cdot 6 \times 980 \times 5600}{273}$$

$$C_p - C_v = \frac{r}{J}$$

$$= \frac{76 \times 13 \cdot 6 \times 980 \times 5600}{273 \times 4 \cdot 2 \times 10^7}$$

$$= 0 \cdot 4946$$

3·11. Specific Heat of a Gas at Constant Volume—Joly's Differential Steam Calorimeter

C is a chamber in which steam can be admitted. P_1 and P_2 are scale pans suspended from the scale pans S_1 and S_2 of a balance.

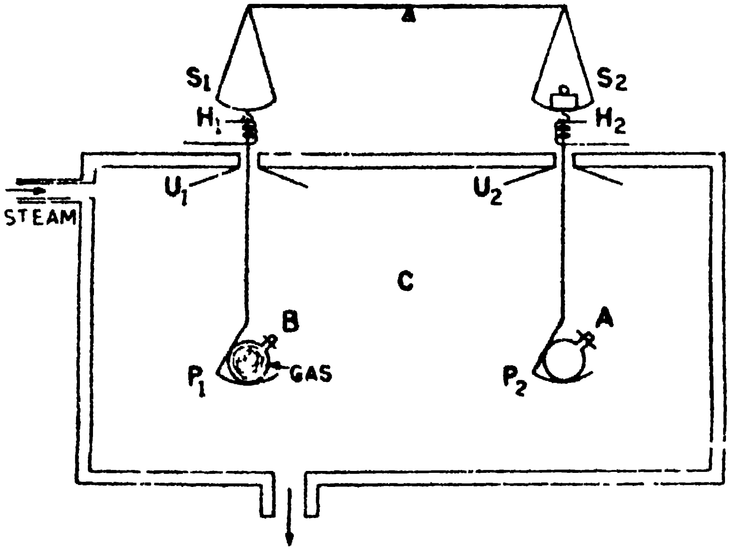


Fig. 3 10

A and B are two identical hollow metal spheres. The two spheres are initially evacuated and by placing them in the pans P_1 and P_2 the balance is counterpoised. In one of the spheres, the gas whose C_v is to be determined is admitted at a pressure of about 10 atmospheres and the balance is counterpoised again Suppose the gas is filled in B. The balance will tilt to the left and the extra mass that has to be kept in the pan S_2 for counterpoising corresponds to that mass of gas enclosed in B (M grams). Now steam is admitted into the chamber and passed continuously till a constant temperature is reached (temperature of steam). Steam condenses and the mass of steam that has condensed on the pan P_1 is more than that condensed on the pan P_2 because in the case of pan P_1 the enclosed gas also has to be heated from the room temperature to the temperature of steam.

The balance tilts and an extra mass has to be kept in the right hand pan to balance it again. This extra mass corresponds to the extra mass of steam condensed on the pan P_1.

The umbrella-shaped vanes U_1 and U_2 will not allow the steam condensed on the rest of the chamber to fall on the scale pans P_1 and P_2. The heating coils H_1 and H_2 will heat the suspension wires to a temperature higher than the temperature of steam and therefore, no steam condenses on these wires.

Suppose,

Mass of the gas $= M$ grams

Sp. heat of gas at constant volume $= C_v$

Initial temperature of the gas $= t_1$°C

Temp. of steam $= t_2$°C

Extra mass of steam condensed on the scale pan $P_1 = m$ grams

Latent heat of vaporisation of water $= L$ cals/g

Heat lost by steam $= mL$

Heat gained by the gas $= MC_v(t_2-t_1)$

$$MC_v(t_2-t_1) = mL$$

$$C_v = \frac{mL}{M(t_2-t_1)} \text{ cals/g·°C}$$

In the second part of the experiment the gas is enclosed in the sphere of pan P_2 and the sphere of pan P_1 is kept empty and C_v is calculated again. The mean of these two values gives the specific heat of the gas at constant volume.

3·12. Specific Heat of a gas at Constant pressure—(Regnault's Method)

The apparatus consists of a reservoir R containing the gas at high pressure and at a constant temperature. The pressure of the gas in the reservoir is shown by the pressure gauge. The apparatus is as shown in Fig. 3·11.

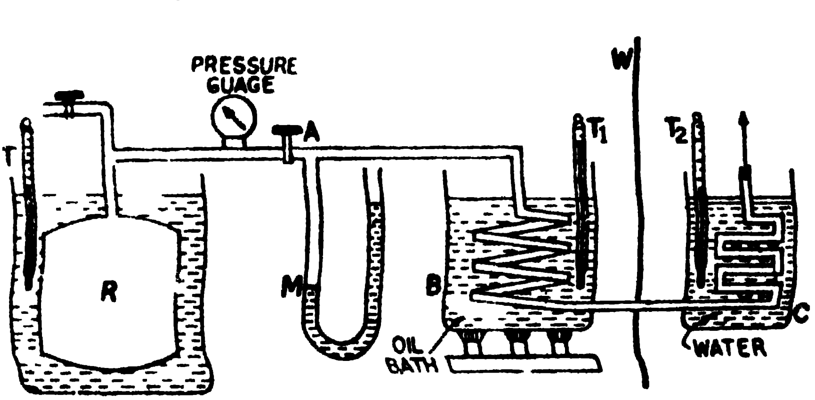


Fig 3·11

The regulator *A* allows the gas to flow at a constant pressure through the spiral tubings immersed in the oil bath *B* and the calorimeter. The pressure of the gas flowing through the spiral tubing is shown by the manometer *M*. Regulator *A* helps in keeping the level of the liquid in the manometer limbs constant.

Suppose the initial pressure of the gas at any instant in the reservoir is P_1, its temperature is T, and volume is V. The temperature shown by the oil bath is T_1 and the calorimeter is at a temperature T_2. Gas is allowed to flow for about half an hour. The gas after passing through the oil bath gets heated to temperature T_1 and after passing through the calorimeter, gets cooled and gives heat to the calorimeter and its contents. Suppose, the final pressure of the gas in the reservoir is P_2, volume is V and the temperature of the calorimeter *C* and its contents is T_3.

Calculations

Suppose, mass of the gas flown $= M$

Mass of water in the calorimeter $= m$

Water equivalent of the calorimeter $= w$

Rise of temperature of calorimeter and its contents

$$= (T_3 - T_2)$$

Mean fall of temperature of the gas

$$= \left(T_1 - \frac{T_2 + T_3}{2} \right)$$

Heat gained = Heat lost

$$(m + w)(T_3 - T_2) = MC_p \left(T_1 - \frac{T_3 + T_2}{2} \right)$$

$$C_p = \frac{(m + w)(T_3 - T_2)}{M\left(T_1 - \dfrac{T_2 + T_3}{2} \right)}$$

To find the mass of the gas (*M*), suppose the density of the gas at NTP $= \rho$. In the experiment, *V* cc of the gas at a pressure $(P_1 - P_2)$ and temperature *T* K has flown through the apparatus. Reducing the volume of the gas to NTP,

$$\frac{(P_1 - P_2)V}{T} = \frac{76\, V_0}{273}$$

or

$$V_0 = \frac{(P_1 - P_2)V \times 273}{76 \times T}$$

$$\therefore \text{Mass } M = V_0 \times \rho = \frac{(P_1 - P_2)V \times 273 \times \rho}{76 \times T}$$

Thus, knowing the value of *M*, C_p can be calculated from equation (*i*).

3·13 Continuous Flow Electrical Method

The specific heat of a gas at constant pressure by electrical method can be determined by using Callendar and Barnes' continuous flow apparatus. Here D is a special glass vessel. The heating coil is at the axis of the vessel. The incoming gas takes a long zig zag path as indicated by the arrow heads (Fig. 3·12).

The reservoir R contains the gas at high pressure and at a constant temperature. The pressure of the gas is read by the pressure gauge. The regulator A allows the gas to flow at a constant pressure through the vessel D. The pressure of the gas flowing through D is indicated by the manometer M. The regulator helps in keeping the pressure of the gas constant throughout the experiment. The filament is heated by electric current. The incoming gas is heated due to the heat generated by the filament. The inlet and the outlet temperatures of the gas are measured with the help of the platinum resistance thermometers T_1 and T'_2.

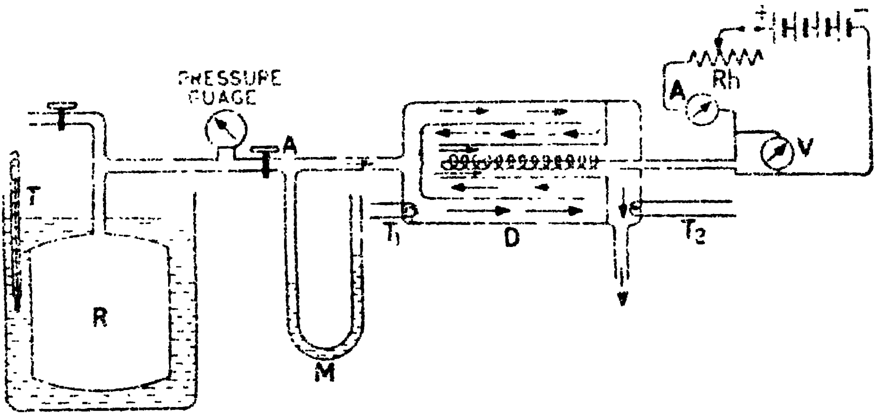


Fig. 3·12

The gas is allowed to flow through the apparatus for some time till the steady state is reached. When the steady state is reached, the thermometers T_1 and T'_2 show constant readings. After the steady state, note the pressure (P_1) of the gas in the reservoir. Allow the gas to flow for half an hour and note the final pressure (P_2) of the gas in the reservoir. During this half an hour, the manometer M and the thermometers T_1 and T_2 should show constant readings.

Calculations

Suppose, the mass of the gas flown $= M$

Temperature of incoming gas $= T_1$

Temperature of outgoing gas $= T_2$

Specific heat of the gas at constant pressure $= C_p$

Voltmeter reading $= E$ volts

Ammeter reading $= I$ amperes

Time $= t$ seconds

Heat produced $= \dfrac{EIt}{4{\cdot}2}$ calories

Heat gained by the gas $= MC_p(T_2-T_1)$

Heat gained = Heat produced

$$MC_p(T_2-T_1) = \frac{EIt}{4{\cdot}2}$$

$$C_p = \frac{EIt}{4{\cdot}2\ M(T_2-T_1)} \qquad \ldots(i)$$

To find the mass of the gas (M), suppose the density of the gas at N T P. = ρ. In the experiment V cc of the gas at a pressure (P_1-P_2) and temperature T has flown through the apparatus. Here V is the volume of the reservoir R. Reducing the volume of the gas to N.T.P.

$$\frac{(P_1-P_2)\,V}{T} = \frac{76\,V_0}{273}$$

$$V_0 = \frac{(P_1-P_2)\,V\times 273}{76\,T}$$

$$\therefore \text{ Mass} \qquad M = \rho V_0 = \frac{\rho(P_1-P_2)\,V\times 273}{76\,T} \text{ grams}$$

Thus knowing the value of M, C_p can be calculated from equation (i).

The chief advantages of this method are :

(1) The temperature of every portion of the apparatus remains constant when the steady state is reached.

(2) The thermal capacity of the flow tube and its contents is eliminated in the calculations.

(3) The loss of heat due to radiation is minimised due to zig-zag path taken by the gas. The gas flows from outer to the inner region of the tube and absorbs any heat radiated from the inner to the outer portion.

(4) The temperatures can be measured accurately under steady state.

(5) The heat produced by electrical arrangement can be calculated accurately.

3·14. Specific heat of a gas at low temperatures

The continuous flow method can be used to determine the specific heat of a gas at low temperature. Before the gas is passed into the tube D, the gas is initially cooled to a desired low temperature. The experiment is performed in a similar way as discussed in article 3·13.

This method is also used to find the specific heat of a gas at different high pressures. In this case, the gas at high pressure is passed through the tube *D*. Scheel and Heuse employed this method to find the specific heat of various gases up to −180°C. Holborn and Jakob used this method to find the specific heat of gases at high pressures.

Molecular Heats of Gases at 20°C

Gas	C_p	C_v
Hydrogen	6·87	4·88
Nitrogen	6·95	4·96
Oxygen	7 03	5·04
Chlorine	8 29	6·15
Air	6·95	4·96
Carbon dioxide	8·83	6 80
Helium	4 97	2·98
Argon	4 97	2·98

The specific heats of hydrogen (for 1 gram) are

$$C_p = 3{\cdot}435 \quad \text{and} \quad C_v = 2\,44$$

3·15. Calorific Value of Fuels

Calorific value of a fuel is defined as the quantity of heat released when a unit quantity of the fuel is completely burnt and the products of combustion are brought to the original temperature. It is expressed as calories per gram or B. T. U. per pound. The fuels commonly used are coal, petrol, spirit, diesel oil, wood etc. The calorific value of different fuels can be determined with the help of a bomb calorimeter.

Bomb Calorimeter. It consists of a vessel *D* made of steel or gun metal. A platinum bowl *B* is suspended inside *D*. The fuel *E* in the form of powder for a solid or a liquid is taken in *B*. A heating wire is immersed in the fuel and its ends are connected to the terminals T_1 and T_2. *R* is a regulating valve for the free supply of oxygen inside *D*. The vessel *D* is closed with an air tight lid. The whole apparatus is immersed in a calorimeter *C* containing water. The fuel is ignited by passing current through the heater wire. The heat produced due to the combustion of the fuel is taken by the surrounding water in the calorimeter.

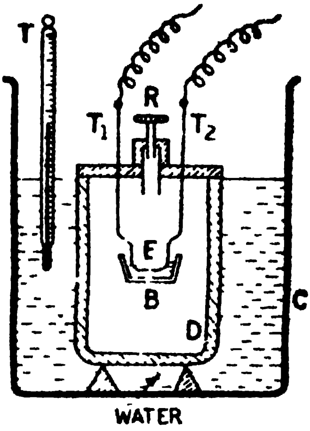


Fig. 3·13

Suppose, the mass of the fuel = *M*

Initial temperature of water $= \theta_1$

Final temperature of water $= \theta_2$

Mass of water $= m$

Water equivalent of the calorimeter and the vessel $D = w$

Heat produced $= (m+w)(\theta_2-\theta_1)$

$\therefore$ Calorific value $= \dfrac{(m+w)\,(\theta_2-\theta_1)}{M}$

3·16 Bell Calorimeter

It is used to find the calorific value of fuels. The apparatus consists of a bell jar *B* arranged inside a calorimeter containing water at room temperature In the crucible *C*, the substance is taken in the powdered form. The leads *L*, *L* are connected to a heating filament dipped inside the fuel in the crucible *C* (Fig. 3·14). *D* is a perforated disc through which the burnt gases inside the bell can escape into water. *A* is a pipe through which oxygen is fed into the combustion chamber.

The fuel is ignited by connecting the leads *L L* to a battery. The fuel burns and the burnt hot gases escape into water in the

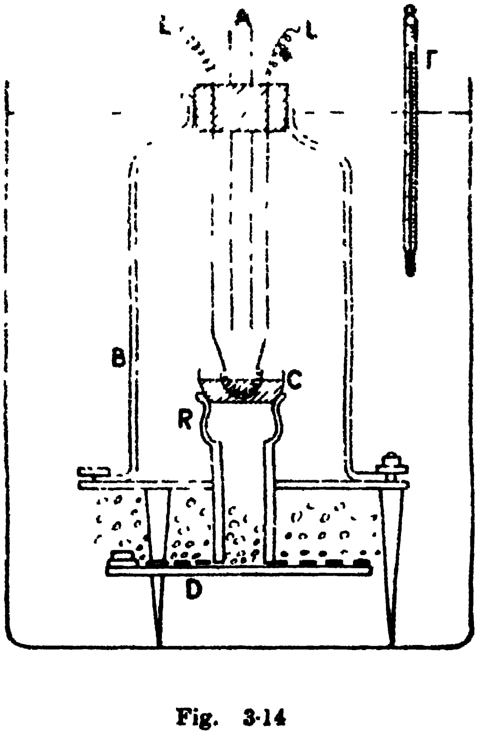


Fig. 3·14

calorimeter, through the disc *D*. When the fuel is completely burnt, the final temperature of water in the calorimeter is noted.

Suppose, the mass of the fuel $= M$
Initial temperature of water $= \theta_1$
Final temperature of water $= \theta_2$
Mass of water $= m$
Water equivalent of the calorimeter $= w$
Heat produced $= (m+w)(\theta_2-\theta_1)$
Calorific value $= \dfrac{(m+w)(\theta_2-\theta_1)}{M}$

Calorific Value of Fuels

Fuel	*Cal/g*
Wood	2500
Gas coke	6000
Methylated spirit	6400
Steam coal	7000
Anthracite coal	8600
Heavy Diesel oil	11000
Petrol	11400
Paraffin oil	11200

Example 3.11. *An engine consumes 25* litres *of gasoline per hour. The calorific value of gasoline is 6×10^6* calories *per* litre. *The output of the engine is 35* kilowatts. *Calculate the efficiency of the engine.*

Total heat produced by gasoline in one hour $= 25 \times 6 \times 10^6$ cals

$$\text{Heat produced per second} = \frac{25 \times 6 \times 10^6}{3600} \text{ cal/s}$$

$$\text{Input} = \frac{25 \times 6 \times 10^6 \times 4.2}{3600} \text{ joule/s i.e., watts}$$

[1 calorie = 4.2 joules]

Output $= 35000$ watts

$$\text{Efficiency} = \frac{\text{Useful output}}{\text{Input}} = \frac{35000 \times 3600}{25 \times 6 \times 10^6 \times 4.2}$$

$$= \frac{1}{5}$$

% efficiency = 20%

3·17 Dulong and Petit's Law

Dulong and Petit, in 1819, studied the specific heat of various elements in a solid state and enunciated a law, called Dulong and Petit's law. According to this law, the *product of the specific heat* *and the atomic weight i.e. atomic heat of all the elements in the solid state is a constant.* The value of this constant was fixed as 6 4 but it is taken as 6 at present. The exact value is 5·96 which also agrees with the value derived from the kinetic theory of matter.

The justification of Dulong and Petit's law was obtained from *Boltzman's consideration of the law of equipartition of energy. According to it, the energy associated with one gram atom of a* substance for each degree of freedom at temperature $T = \frac{1}{2} RT$. Here R is the universal gas constant. If the atom is considered to be vibrating about the mean position, its mean kinetic energy will be equal to its mean potential energy.

For each form of energy there are three degrees of freedom. Therefore an atom has got six degrees of freedom. Thus the total energy associated with one gram atom of a substance at a temperature $T = 3RT$

$$\therefore \qquad U = 3RT$$

$$A_H = \frac{dU}{dT} = 3R$$

A_H is the atomic heat of the substance

$$A_H = \frac{3 \times 8{\cdot}31 \times 10^7}{4{\cdot}18 \times 10^7} \text{ cals/g-atom-K}$$

$$A_H = 5{\cdot}96 \text{ cals/g-atom-K}$$

Atomic Heat of Substances at 20°C

Substance	*Atomic Weight*	*Specific Heat*	*Atomic Heat*
Aluminium	27·0	0·212	5·72
Boron	10·8	0·307	3·32
Carbon	12·0	0·160	1·92
Copper	63·6	0·091	5 79
Gold	197·2	0·031	6 11
Iron	55·8	0 110	6·12
Lead	207·2	0·030	6·21
Silicon	28·1	0·182	5·11
Silver	107·9	0·056	6·04
Zinc	65 4	0.092	6·02

Dulong and Petit's law was modified by Woestyn for metallic compounds. According to him, the *molecular heat of a compound* is equal to the sum of the atomic heat of its constituents. Further, it was found by Newmann that the molecular heat of the compounds of similar nature is also constant. The molecular heat in the case of NaCl, AgCl and KCl was found to be nearly 13 and that of Sb_2O_3, Fe_2O_3, As_2O_3 was found to be equal to 26.

3·18 Variation of Specific Heat and Atomic Heat with Temperature.

It is found that Dulong and Petit's law is not true in the case of carbon, boron and silicon. In the case of these elements the atomic heats at 20°C are 1·92, 3·32 and 5·11. These values differ from the constant value of 6. This variation in atomic heat could not be explained on the basis of kinetic theory of matter. However, it was found by Nernst that the specific heat of a substance decreases with decrease in temperature and at absolute zero the specific heat tends to be zero. Further, he was able to show that the specific heat increases with the rise in temperature and tends to a maximum value. Therefore, the atomic heat of a substance tends to a maximum value of six and decreases with decrease in temperature. In the case of carbon, boron and silicon also, the atomic heat is 6 at high temperatures (Fig. 3·15).

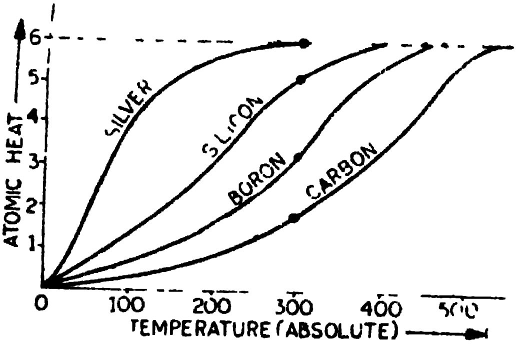


Fig. 3·15

In the case of silver, the atomic heat is 6 at room temperature but it is also less than 6 at lower temperatures.

Atomic Heats of Silver at Low Temperature

Temperature (K)	*Atomic heat*
205	5·61
144	5·37
103	4·80
75	4·04
56	3·19
36	1·69
20	0·40
10	0·05
5	0·005
1·4	0·00025

3·19 Quantum Theory

Dulong and Petit's law has been explained on the basis of quantum theory of heat radiation. According to quantum theory, heat is radiated in the form of discrete particles called photons. Each particle has energy equal to $h\nu$ where h is the Planck's constant and ν is the frequency of heat radiations. Einstein also explained Dulong and Petit's law on the basis of quantum theory and said that the ato[illegible] heat is equal to 6 only at higher temperature, and this is the m[illegible]mum value. The atomic heat of the elements decreases with de[illegible] temperature. Most of the substances reach the maximum v[illegible] of 6 at room temperature but carbon, [illegible] and silicon are [illegible] maximum value of six at room temperature. The atomic [illegible] tend to the maximum value of 6 at high temperature.

Debye [illegible] modified Einstein's theory and concluded that in some substances like copper, aluminium, iron etc., the atomic heat at low temperature decreases more slowly than explained by Einstein.

A[illegible] to Debye Einstein theory

(a) The atomic heat of all the elements tends to the maximum value 6.

(b) The [illegible] heat of all the elements decreases with the fall of temperature.

(c) [illegible] heat tends to the value zero, near about absolute zero.

(d) A[illegible] temperature, the atomic heat varies as the cube of absolute temperature.

Atomic heat ∝ T^3

[illegible] T^3 a[illegible]

[illegible] between atomic heats and absolute tem[illegible] will coincide if the temperature scale is suitably modified according to the expression,

$$A = f\left(\frac{\theta}{T}\right)$$

Here, A is the atomic heat of the element at absolute temperature T and θ is a parameter called Debye temprature. Debye temperature is a constant for a particular element but is different for different elements. The value $f\left(\frac{\theta}{T}\right)$ is the same for all the elements at absolute temperature T. Thus according to this theory a single graph between A and $f\left(\frac{\theta}{T}\right)$ for all the elements is obtained (Fig 3·16).

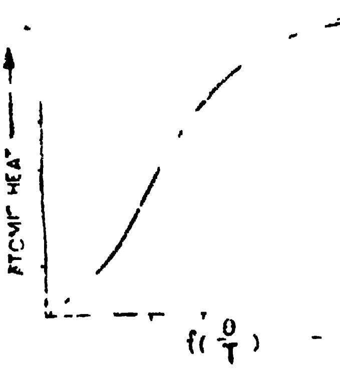


Fig. 3·16

Exercises III

1. Describe the continuous flow calorimeter. What are the advantages of this method ? How do you determine C_p of a gas by using this method ? *(Delhi 1969 ; Agra 1961)*

2. Describe fully the working of the continuous flow calorimeter of 'Callendar and Barnes' What are the advantages of this method ? What information has it given regarding the specific heat of water ? *(Agra 1963 ; Delhi 1971)*

3. Derive an expression for the difference in the two specific heats of a gas *(Agra 1966)*

4 Describe and explain Joly's steam calorimeter method for finding the specific heat of a gas at constant volume. *(Agra 1966)*

5 Point out the difference between the two principal specific heats of a gas and show that for an ideal gas

$$C_p - C_v = R$$

(Lucknow 1961 ; Delhi 1972)

6 Describe the bomb calorimeter method to find the calorific value of a fuel. *(Lucknow 1972)*

7 Indicate the manner in which the specific heat of a solid varies with temperature and outline the theory which explains this variation

8 Discuss Newton's law of cooling How will you determine the specific heat of a liquid by Newton's law of cooling ?
[*Delhi (Add Physics) 1975* , (*Delhi 1973*)]

9 Describe the Regnault's method to find the specific heat of a gas at constant pressure

10 Describe [illegible] of a bomb calorimeter in determining the calorific value of a fuel

11 Discuss Dulong and Petit's law and explain the variation of the atomic heat of a substance with temperature.

12 How do you explain Dulong and Petit's law according to quantum theory of radiation.

13 Discuss Debye-Einstein theory regarding atomic heats of solids. Discuss Debye's T^3 law. *(Madras 1974)*

14 Deduce the relation between the specific heat of a gas at constant pressure and at constant volume. *(Delhi 1968)*

15. Describe how the specific heat of a gas at constant pressure is determined accurately. *(Delhi 1968)*

16. Describe Nernst vacuum calorimeter and indicate briefly how it may be used to determine the specific heat at low temperatures. *(Delhi 1972, 1974)*

17. Describe fully the working of a continuous flow electric calorimeter for the measurement of C_p of a gas. *(Delhi [illegible])*

18. Distinguish between the specific heat of a gas at constant pressure and at constant volume. Describe an accurate method to determine the specific heat of a gas at constant pressure. *(Delhi, 1976)*

19. Describe Joly's differential steam calorimeter. How will you use this apparatus for determining the specific heat of a gas at constant volume ? Mention the sources of error. *(Delhi, 1976)*

20. Point out the difference between the two principal specific heats of a gas. Describe an accurate method to determine the specific heat of a gas at constant pressure. *(Delhi, 1976)*

21. State and explain Newton's law of cooling. How will you find the specific heat of a liquid by the method of cooling ? *(Delhi, 1976)*

22. Describe Nernst vacuum calorimeter for determining the specific heat of a good-conducting solid at low temperatures. *[Delhi, 1978]*

23. Describe the nature of variation of specific heat of solids with temperature. Discuss important regions of this curve. *[Delhi, 1978]*

24. A liquid takes 10 minutes to cool from 90°C to 60°C How much time will it take to cool from 70 C to 40°C ? The temperature of the surroundings is 30°C. [**Ans.** 20 minutes]

25. A body takes 6 minutes to cool from 80°C to 50°C. How much time will it take to cool from 60°C to 30°C ? The temperature of the surroundings is 20°C. [**Ans.** 12 minutes]

26. A body cools from 70°C to 50°C in 6 minutes. What will be its temperature after the next 6 minutes ? The temperature of the surroundings is 15°C. [**Ans.** 32·27°C]

27 A liquid cools in 7 minutes from 60°C to 40°C. What will be its temperature after the next 7 minutes ? The temperature of the surroundings is 10°C. [**Ans.** 28°C]

28. A liquid takes 5 minutes to cool from 70°C to 50°C. How much time will it take to cool from 50°C to 35°C ? The temperature of the surroundings is 20°C. [**Ans.** 6·785 minutes]

29. A body takes 3 minutes to cool from 70°C to 60°C. What will be its temperature after the next 6 minutes ? The temperature of the surroundings is 25°C. [**Ans.** 46·17°C]

30. A liquid takes 4 minutes to cool from 65°C to 50°C. What will be its temperature after the next 10 minutes ? The temperature of the surroundings is 35°C. [**Ans.** 37·65°C]

31. A petrol engine consumes 25 kg of petrol per hour. The calorific value of petrol is $11{\cdot}4 \times 10^6$ cals per kg. The power of the

engine is 99·75 kilowatts. Calculate the efficiency of the engine.
[**Ans.** 30%]

32. A Nernst calorimeter of lead weighing 396·3 grams and surrounded by a bath at temperature 61 K, on being heated electrically for four minutes showed a rise in temperature of 1·219 K under condition of no heat leakage. Calculate the atomic heat of lead at 61 K, if the potential drop and average current during the interval of heating were 1·586 volts and 0·1444 ampere respectively. (Atomic weight of lead = 206·4 and J = 4·18 joules/calorie.) (*Delhi 1972*)
[**Ans.** 5·619]

33. A copper calorimeter of mass 100 g containing 150 cm^3 of a liquid of specific heat 0·6 and specific gravity 1·2, is found to cool at the rate of 2°C per minute when its temperature is 50°C above that of the surroundings. If the liquid is emptied out and 150 cm^3 of a second liquid of specific heat 0·4 and specific gravity 0·9 are substituted, what will be its rate of cooling, when the temperature is 40°C above that of its surroundings ? (Sp. heat of copper 0·1.)
(*Delhi 1973*) [**Ans.** 2·76°C per minute]

4

Change of State

4.1 Change of State

A substance can exist in three states, *viz.*, solid liquid and gas. The particular state of a substance depends on its temperature. According to the kinetic theory the molecules of a substance in the solid state have less degrees of freedom than a substance in the liquid or gaseous state. The molecules are more free to move in the gaseous state. The change of state can be brought about by supplying or withdrawing heat from the substance. Ice is the solid state of water. By supplying heat to ice it can be changed into water. Similarly by supplying heat to water it can be converted into the gaseous state (vapour). The reverse processes occur when heat is withdrawn from steam. This is true for all substances. Even permanent gases like oxygen, nitrogen, hydrogen etc. can be liquefied at low temperature.

For a given substance, the change of state takes place at a fixed temperature and at a given pressure and *vice versa*. When the substance changes from the solid to the liquid state, the heat supplied at constant temperature (called melting point) is used in overcoming the force of intermolecular attraction. The mean molecular distance increases and the molecules are more free to move. Similarly, when the substance changes from the liquid to the gaseous state at a fixed temperature (called the boiling point) at standard atmospheric pressure, the heat supplied is used in increasing the mean molecular distance. The molecules become free to move about in the whole space available to them.

4.2 Latent Heat of Fusion

Take small pieces of ice in a beaker. Fix a thermometer to note the temperature of ice in the beaker. Heat the beaker slowly. Ice melts but the thermometer does not show any rise in temperature. When the whole ice has melted the temperature of water rises and it is indicated by the thermometer. During the processes of conversion from ice to water (change of state from solid to liquid) the heat supplied is used to change the state of ice from solid state to liquid state. This heat is called latent heat. Latent means hidden *i.e.* which is not indicated by the thermometer.

It has been found that one gram of ice takes 80 calories of heat to get itself converted to water. This heat is called latent heat of fusion of ice. Its unit is cals/gram

Latent heat of fusion of a substance is defined as the amount of heat required to change the state of one gram of a substance from solid to liquid without any change in its temperature.

The melting point of ice is 0°C at a pressure of 76 cm of Hg.

4·3 Laws of Fusion

(1) Every substance changes its state from solid to liquid at a particular temperature (under normal pressure) called the melting point.

(2) As long as the change of state takes place, there is no change in temperature.

(3) One gram of every substance requires a definite quantity of heat for change of state from solid to liquid and it is called the latent heat of fusion of that substance. It is different for different substances.

(4) Some substances show increase in volume on melting *e.g.* wax, ghee etc. while some other substances show decrease in volume on melting *e.g.*, ice.

(5) The melting point of those substances which decrease in volume on melting, is lowered with increase in pressure.

(6) The melting point of those substances which increase in volume on melting, is increased with increase in pressure.

Note. (1) Ice decreases in volume on melting and its melting point is lowered with increase in pressure.

(2) The melting point or solidification point is the same for a substance.

4·4 Practical Applications

(1) Aquatic animals live underneath water in ponds and lakes in winter. Ice is formed on the surface of the pond, and it remains on the surface due to its increase in volume and hence lesser density.

(2) Rocks in the mountains break in frosty weather. Water, which may be locked up in the pores of the rock, may freeze into ice and there is increase in volume. This produces cracks in the rocks.

(3) Fertility of the soil increases due to the splitting of the soil in frosty weather. Water freezes into ice and there is increase

in volume. This increase in volume of ice disintegrates the soil.

(4) Alloys which expand on solidification are used for better casting The alloy in the liquid form is put into the cast When it solidifies, there is increase in volume and a sharp casting is obtained Type metal expands on solidification.

4·5 Effect of Pressure on Freezing Point of Ice—Regelation

Melting point of ice is lowered with increase in pressure. Take a slab of ice. Take a wire and fix two weights (5 kg each) at its two ends Put the wire over the slab as shown in Fig. 4·1.

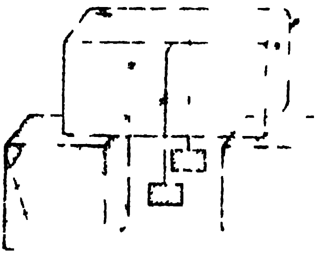


Fig 4·1

The wire passes through the ice slab Just below the wire, ice melts at a lower temperature due to increase in pressure When the wire has passed the water above the wire freezes again Thus the wire passes through the slab and the slab does not split This phenomenon of refreezing is called *Regelation*

In a similar way it is possible to freeze two pieces of ice by applying pressure and then releasing them

Examples. (1) Water pipes burst in winter in cold countries due to solidification of water into ice When water is converted into ice there is increase in volume and the pipes are likely to burst

(2) When wheels of a cart pass over snow, it melts due to increase in pressure exerted by the wheels When the wheel passes over, the water formed on the wheel solidifies due to regelation Due to this reason wheels are covered with snow

(3) Skating is possible on snow due to the formation of a thin layer of water formed below the skates. The water is formed due to the increase of pressure and it acts as a lubricant

4·6 Impurities lower Freezing Point

When salt is mixed with ice, some ice melts taking heat from the salt The temperature of the mixture decreases. Further, the salt dissolves in the water formed and takes latent heat from the mixture The temperature of the mixture is decreased further. In this way, with a freezing mixture of salt and ice in the ratio 1 3, temperatures as low as —13°C can be obtained A freezing mixture consists of powdered ice, common salt and ammonium nitrate

Similarly when sugar is dissolved in water, the water is cooled

4·7 Determination of Melting Point of Wax

Take sufficient quantity of wax in a test tube and fix a cork along with a thermometer. Adjust the test tube in a beaker containing water (Fig. 4·2). Heat the water to its boiling point. The wax in the test tube melts and is in the liquid state. Extinguish the burner and allow the water and wax to cool. Note the temperature of wax after every one minute till the temperature of wax is about 30°C. Draw a graph between temperature and time. The temperature corresponding to the horizontal line in the graph gives the melting point of wax. At this temperature, liquid wax is converted into the solid wax without change of temperature (Fig. 4·3).

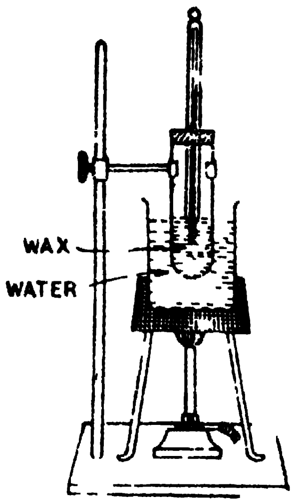


Fig. 4·2

Plot a graph between temperature along the *Y* axis and time in minutes along the *X*-axis.

The temperature corresponding to the line *BC* gives the melting point of wax. The portion *AB* shows the liquid state of wax and below *C* the graph represents the solid state.

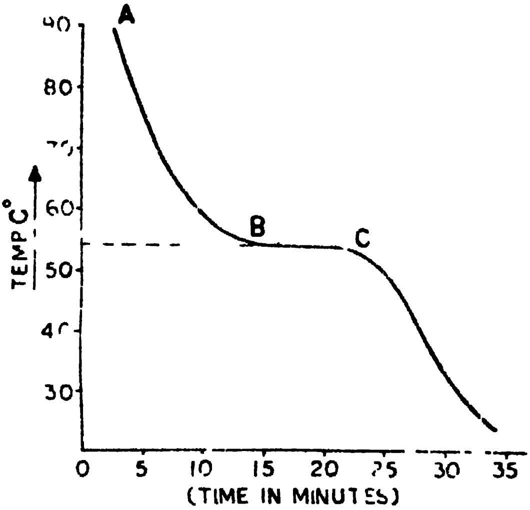


Fig. 4·3

4·8 Determination of Latent Heat of Fusion of Ice

Take a calorimeter. Weigh the calorimeter along with the stirrer. Weigh the calorimeter with stirrer and the lid. Heat some water in a beaker to a temperature of about 10°C higher than t room temperature. Fill the calorimeter to about half, with hot water. Weigh the calorimeter, hot water, stirrer and lid. Place it in a wooden box. Note the temperature of water in the calorimeter. It should be about 4 to 5°C higher than the room temperature. Take small pieces of ice in a blotting paper. Add dry pieces of ice gradually into the calorimeter and stir. Continue adding dry pieces of ice into the calorimeter, till the temperature of water is about 4 to 5 °C lower than the room temperature. (This is done to avoid radiation error). Note the final temperature and weigh the whole contents. See that before recording the final temperature the whole of ice has melted.

When one gram of ice melts into water at 0°C, the amount of heat absorbed is called the latent heat of fusion of ice. Suppose M grams of ice is added to m grams of water at t°C in a calorimeter whose water equivalent is W. The final temperature reached $= T$°C.

Heat lost by water and calorimeter $= (m+W)(t-T)$

$\therefore$ Heat gained by ice

$$= ML + MT$$

$$\therefore \quad \text{Heat gained} = \text{Heat lost}$$

$$ML + MT = (m+W)(t-T)$$

$$L = \frac{(m+W)(t-T)}{M} - T$$

Hence latent heat of fusion of ice can be determined.

4·9 Heat Absorbed in Solution

When a solution is formed by dissolving a solute (solid substance) in a solvent (liquid) the following possible changes take place.

(1) The solute gets dissolved in the solvent and takes the necessary latent heat from the solvent. The temperature of the solution decreases. However, in some rarer cases there is absorption of heat.

(2) When a solute is dissolved in a solvent, a chemical reaction may take place. This reaction is generally accompanied by evolution of heat.

(3) When an electrolyte is dissolved in water *e.g.* $CuSO_4$ dissolved in water, ionic dissociation takes place. In this process heat is absorbed.

However, depending on the nature of the substance *i.e.* solute and the solvent, the total effect may be absorption or evolution of heat.

4·10 Vaporization and Condensation

The conversion of a substance from the liquid to the vapour state is called *vaporization.* Boiling is the phenomenon of vaporization accompanied by ebullition *i.e.*, violent ebullition of bubbles. However vaporization can take place without boiling. The water kept on an open plate in summer evaporates and there is a change of state. But there is no boiling. Conversion of water to steam is vaporization. The conversion of the substance from the vapour state to the liquid state is called condensation. Conversion of steam into water is called condensation. Rain is caused due to the condensation of water vapour in the clouds.

4·11 Laws of Ebullition or Boiling

(1) Every liquid changes its state from liquid to its vapour at a particular temperature (under normal pressure) called the boiling point.

(2) As long as the change of state takes place, there is no change in temperature.

(3) One gram of every liquid requires a definite quantity of heat for change of state from liquid to vapour and it is called the latent heat of vaporization of that liquid. Latent heat is different for different substances.

(4) All liquids show increase in volume on vaporization

(5) The boiling point of a liquid increases with increase in pressure of a liquid.

(6) The liquid can boil at a lower temperature under reduced pressure.

4 12 Change in Boiling Point with Pressure

The effect of pressure on the boiling point (saturation temperature) of a liquid can be studied with the help of the apparatus shown in Fig. 4·4 The temperature at which the change of state from liquid to vapour takes place is called saturation temperature. The saturation temperature increases with increase in pressure. If the pressure is 1 atmosphere, the saturation temperature is called the boiling point. The vessel *A* contains the liquid (say water). It is connected to the flask *B* through a tube *C* surrounded by a water condenser To measure the pressure of air over the surface of the liquid in *A*, a manometer is used.

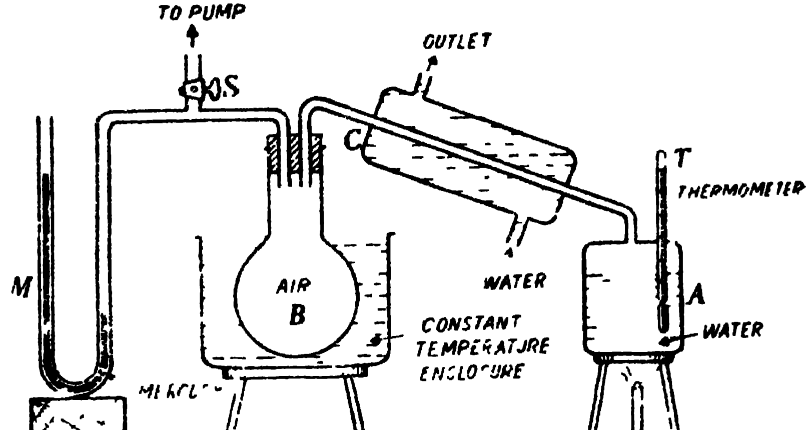


Fig. 4·4

The pressure of air inside *A* and *B* can be changed with the help of the compression pump or evacuation pump.

The stopcock S is opened. With the help of the compression pump, air is compressed into B. The stopcock is closed. Pressure of air in A and B is shown by the manometer. It is more than the atmospheric pressure.

The liquid is heated and the temperature at which it boils is recorded by the thermometer. At the boiling point, the temperature of the liquid remains constant. The condenser through which cold water is circulated prevents steam to enter the vessel B. The steam is condensed and condensed water flows back to A.

In this way at various pressures, the corresponding boiling points of the liquid can be determined. For low pressure, the vacuum pump is used. It is found that the boiling point of a liquid increases with increase in pressure and decreases with decrease in pressure.

The boiling point of water at 76 cm of Hg pressure is 100°C. The boiling point of water at double the normal pressure (*i.e.*, 152 cm of Hg) is about 128°C.

Applications

Papin's Digestor and Pressure cookers are based on the principle that the boiling point of a liquid increases with increase in pressure.

The pressure inside the pressure cooker is much higher than the atmospheric pressure. The steam produced inside the cooker is not allowed to escape and the pressure over the surface of water increases. It means water inside the vessel will be at a temperature higher than the normal boiling point. Vegetables cooked with a pressure cooker are prepared in a short time.

When the pressure increases beyond the desired pressure, the weight placed on the lid lifts up a little and allows the steam to escape slowly and maintains constant pressure inside it. For safety purposes, a safety valve is also provided on the lid. The safety valve on a pressure cooker is a fusible plug. In case, the weight fails to lift, the pressure inside the cooker may increase enormously and may lead to explosion. To prevent this, a fusible plug is provided. It has a small stem made of a material of low melting point. When the pressure inside increases, the saturation temperature also increases and the plug melts. Due to this the steam escapes and the pressure inside the cooker gets lowered.

When a pressure cooker is kept on a stove, on filling it with water to the normal level, vaporization takes place. The water starts evaporating at temperatures lower than the boiling point temperature because of the pressure of air and hence the actual pressure of evaporation is the difference between the atmospheric pressure and the partial pressure of air. As the temperature increases, the rate of evaporation increases and the air is expelled. Gradually, due to the expulsion of air, the vapour pressure of water increases and hence the temperature. After all the air is expelled, boiling takes place. The steam starts rushing out through the opening.

The weight is now placed on the opening. Further, steam that is produced increases the pressure and hence the boiling point is also raised. As soon as the upward force due to the steam pressure is sufficiently high, the weight lifts and allows the steam to escape. This maintains constant pressure and hence constant temperature. If the weight is placed before the expulsion of steam, the partial pressure will not be as high as it ought to be and hence the temperature is not high.

4·13 Franklin's Experiment

Take a flask containing water. Heat it till the water begins to boil. When the water is boiling, the air escapes to the atmosphere. After some time, close the mouth of the flask with an air tight rubber cork. Invert the flask and fix it on the retort stand (Fig 4 5). Pour cold water over the flask. Due to the condensation of steam, the pressure over the surface of water decreases. Water inside the vessel begins to boil. This experiment shows that water boils at a lower temperature under reduced pressure.

In the laboratory, while preparing steam, the temperature of steam is usually less than 100°C because the atmospheric pressure is less than 76 cm of Hg.

Fig. 4·5

4 14 Latent Heat of Vaporization

latent heat of vaporization of a liquid is the amount of heat required to convert one gram of a liquid into vapour without any change in temperature. For water, latent heat of vaporization is 537 cals/gram at a pressure of 76 cm of Hg. Latent heat of vaporization is different for different substances.

Determination of latent heat of steam

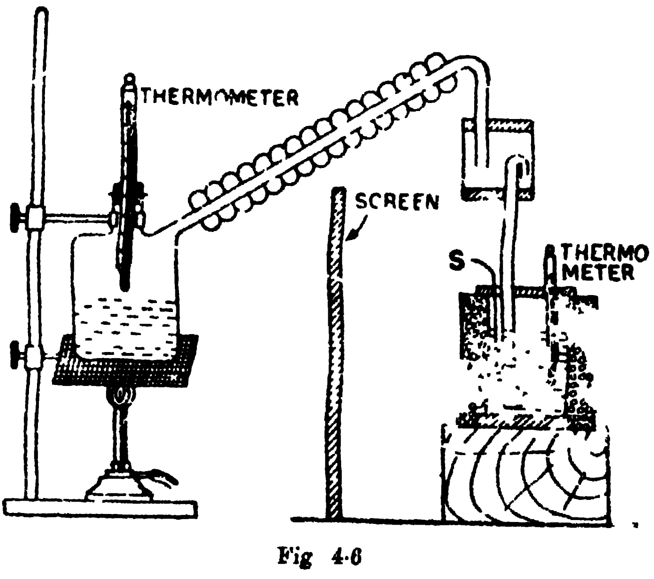


Fig 4·6

Take a calorimenter. Weigh the calorimeter along with the stirrer. Weigh the calorimeter along with the stirrer and the lid. Fill the calorimeter to about 2/3 with water and weigh along with the stirrer and the lid. Heat the water in the boiler to produce steam. The boiler is fitted with a steam trap as shown in Fig. 4·6. The whole of the delivery tube is covered with wool. When steam starts coming out of the end of the tube, note the temperature of steam. Note the temperature of water in the calorimeter. Now clean the end of the tube with a blotting paper to remove water drops. Insert the tube quickly into the calorimeter and pass steam. When the temperature of water is raised through about 10°C, take out the tube carefully. Continue stirring. Note the final temperature. Remove the thermometer carefully and weigh the calorimeter. The calorimeter should be covered with a lid and no water drops should be sticking to the thermometer

Suppose, m grams of steam is passed into M grams of water at t_1°C in a calorimeter of water equivalent w. The temperature of steam is t_2°C and final temperature is T°C.

Heat gained by water and calorimeter $= (M+w)(T-t_1)$

Heat lost by steam $= mL+m(t_2-T)$

Heat gained $=$ Heat lost

$$(M+w)(T-t_1) = mL+m(t_2-T)$$

$$L = \frac{(M+w)(T-t_1)}{m}-(t_2-T)$$

Hence, latent heat of steam can be determined.

Example 4·1. *One kilogram of ice at —10°C is heated until the whole of it evaporates. How much heat is required ? Latent heat of fusion of ice = 80 cals per gram and that of steam = 540 cal per gram.*

Mass of ice = 1 kg = 1000 g

Sp heat of ice = 0·5 cal/g- K

(1) Heat required to raise the temperature of ice

from —10°C to 0°C = 1000×0·5×10 = 5000 cals

(2) Heat required to melt ice at 0°C

= 1000×80 = 80000 cals

(3) Heat required to raise the temperature of water

from 0°C to 100°C = 1000×100 = 100000 cals

(4) Heat required to convert water into steam at 100°C

= 1000×540 = 540000 cals

Total quantity of heat required

= 5000+80000+10000+540000

= **725000 cals**

Example 4·2. *One gram of steam is passed into a calorimeter containing 100 grams of ice. Calculate the amount of ice melted.*

Heat given out by one gram of steam when converted from steam into water at 100°C $= mL = 1 \times 537 = 537$ cal.

Heat given out by one gram of water when cooled from 100°C to 0°C

$$= 1 \times 100 = 100 \text{ cal}$$

∴ Total quantity of heat given out by one gram of steam

$$= 537 + 100 = 637 \text{ cal}$$

Suppose the amount of ice melted

$$= m \text{ grams}$$

Latent heat of ice $= 80$ cal per gram

Heat absorbed by ice

$$= 80\,m \text{ cal}$$

Heat lost by steam = Heat gained by ice

$$\therefore \quad 637 = 80\,m$$

or

$$m = \mathbf{7{\cdot}96\ g}$$

Example 4·3. *What will be the result of adding 52 g of ice to 100 g of water at 40°C?*

Mass of water $= 100$ g

Temperature of water

$$= 40°\text{C}$$

∴ Heat lost by water when its temperature falls from 40°C to 0°C $= 100 \times 40$

$$= \mathbf{4000\ cal}$$

If 52 g of ice melts, heat gained by it should be $52 \times 80 = 4160$ calories. But water can lose only 4000 calories of heat. Therefore, the whole of ice will not melt.

∴ Amount of heat gained by ice

$$= 4000 \text{ cal}$$

Amount of ice that melts

$$= \frac{4000}{80} = 50 \text{ g}$$

Remaining ice $= 52 - 50 = 2$ g

Hence the result will be 2 g of ice and 150 g of water at 0°C.

Example 4·4 *It takes fifteen minutes for an electric kettle to heat a certain quantity of water from 0°C to the boiling point 100°C. It requires 80 minutes to turn all the water at 100°C into steam. Determine the latent heat of steam. (Assume the radiation losses to be neglegible).*

Suppose mass of water $= m$

Heat required to raise its temperature from 0°C to 100°C

$$= 100\,m$$

∴ Heat produced by electric kettle in 15 minutes $= 100\,m$

Heat produced by electric kettle in 1 minute

$$= \frac{100\ m}{15}$$

Heat produced by electric kettle in 80 minutes

$$= \frac{100\ m \times 80}{15}\ \text{cal}$$

Suppose latent heat of steam $= L$ cal per gram

Heat required by m grams of water to boil off into steam

$$= mL\ \text{cal}$$

$$\therefore \qquad mL = \frac{100\ m \times 80}{15}$$

or $$L = \mathbf{533{\cdot}33\ cal/g}$$

Example 4 5. *A refrigerator converts 50 g of water at 15°C into ice at —20°C in one hour. Determine the quantity of heat removed per* minute. (*Specific heat of ice* $= 0{\cdot}5$)

Here $m = 50$ g

Heat removed in cooling water from 15°C to 0°C

$$= 50 \times 1 \times 15 = 750\ \text{cal}$$

Heat removed in converting water into ice at 0°C

$$= 50 \times 80 = 4000\ \text{cal}$$

Heat removed in cooling ice from 0°C to —20°C

$$= 50 \times 0{\cdot}5 \times 20 = 500\ \text{cal}$$

Total heat removed in one hour

$$= 750 + 4000 + 500 = 5250\ \text{cal}$$

Heat removed per minute

$$= \frac{5250}{60}$$

$$= \mathbf{87{\cdot}5\ cal/minute}$$

4·15 Bunsen's Ice Calorimeter

Bunsen's ice calorimeter is used to find the specific heat of a solid or a liquid available in a small quantity. It is based on the principle that when ice melts there is decrease in volume. When one gram of ice melts, the decrease in volume is 0 09 cc.

The apparatus consists of a metal calorimeter C fitted inside a bulb B. The bulb B is connected to the cup A through a glass tube. The cup A is fitted with an air tight lid. A capillary tube EF is fixed whose one end dips inside mercury in the cup A The horizontal portion of the capillary tube is fitted on a graduated scale. The upper portion of the bulb B contains water at 0 C. The lower portion of B, the connecting tubes and the cup A contain mercury.

By adjusting the position of the screw T the position of the mercury meniscus in the capillary tube EF can be suitably adjusted. The whole apparatus is enclosed in a bath of melting ice.

Working. Ether is poured in the calorimeter C. It evaporates and takes heat for evaporation from the surrounding water in B As water in B is already at 0°C, a small quantity of water surrounding C freezes into ice.

The substance whose specific heat is to be determined is heated to a desired temperature (θ°C). The position of mercury in the capillary EF is noted on the scale.

The substance is transferred quickly into the calorimeter C The calorimeter is closed with the rubber cork The substance loses heat to the surrounding ice and cool to 0°C. A small quantity of ice melts and there is decrease in volume Consequently the mercury in the capillary tube EF recedes Suppose the length through which mercury has moved $= l$ cm and area of cross-section of the capillary tube $= a$ sq cm

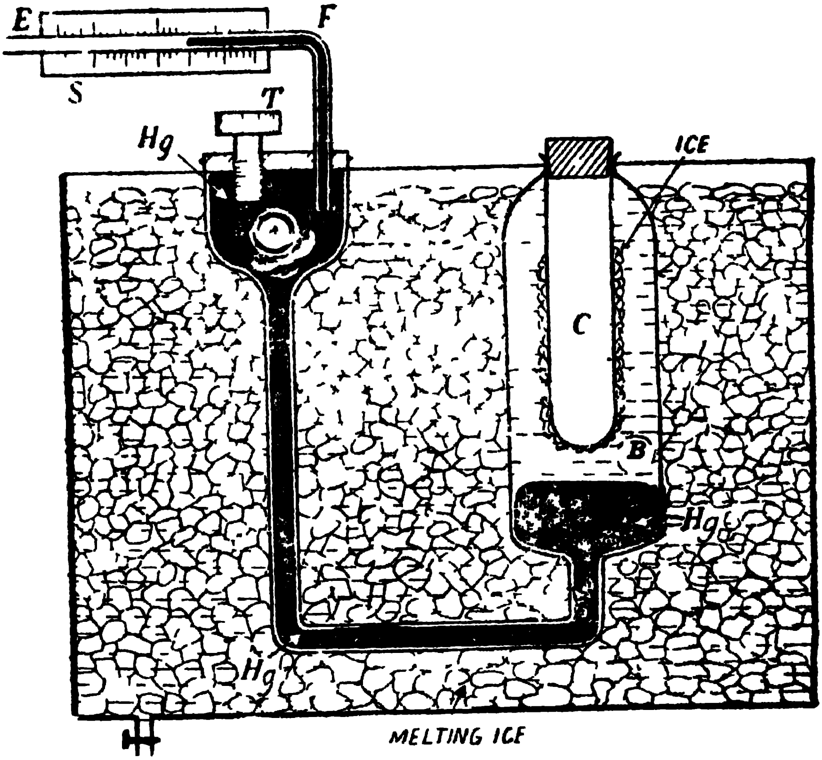


Fig 4.7

$\therefore$ Decrease in volume $= v = al$

When decrease in volume is 0·09 cc the amount of ice that melts

$= 1$ gram

When decrease in volume is v cc the amount of ice that melts

$$= m = \frac{v}{0{\cdot}09} \text{ grams}$$

Latent heat of ice $= 80$ cal/g

Heat gained by ice $= 80\, m = \dfrac{80\, v}{0{\cdot}09}$ cal

Heat lost by the substance

$$= MS\,\theta$$

Heat lost = Heat gained

$$\therefore \quad MS\,\theta = \frac{80\, v}{0{\cdot}09}$$

or

$$S = \frac{80\, v}{0{\cdot}09\, M\theta} \text{ cal/g-°C} \qquad \ldots(i)$$

Advantages :

(*i*) This method is accurate and sensitive.

(*ii*) It is suitable to find the specific heat of a substance available in small quantity.

(*iii*) Water equivalent of the calorimeter does not come into the calculation as the calorimeter remains at 0°C throughout.

(*iv*) There is no need to note the final temperature.

(*v*) There is no loss of heat by radiation or conduction.

Example 4 6. *20* g *of a substance at 100°C, placed in the tube of a Bunsen's ice calorimeter, moves the mercury in the capillary tube 1* sq mm *area through 50* mm. *Find the specific heat of the substance if 1000* cc *of water becomes 1090* cc *of ice on freezing.*

1000 cc of water becomes 1090 cc of ice on freezing.

It means 1000 g of ice on melting decreases in volume by

$$1090 - 1000 = 90 \text{ cc}$$

i.e., when one gram of ice melts decrease in volume

$$= \frac{90}{1000} = 0{\cdot}09 \text{ cc}$$

Mass of the substance

$$= M = 20 \text{ g}$$

$$\theta = 100\text{°C}, \qquad S = ?$$

Area of cross-section $= a = 1$ sq mm

$$= \frac{1}{100} \text{ sq cm}$$

Length of the column through which liquid moves

$$= 50 \text{ mm} = 5 \text{ cm}$$

$$\text{Decrease in volume} = v = l \times a = 5 \times \frac{1}{100}$$

$$= \frac{1}{20}\ \text{cc}$$

$$MS\theta = \frac{80\,v}{0\cdot 09}$$

$$S = \frac{80\,v}{0\cdot 09 \times M \times \theta}$$

$$= \frac{80 \times 1}{20 \times 0\cdot 09 \times 20 \times 100}$$

$$= \mathbf{0\cdot 022\ cal/g\text{-}^\circ C}$$

Example 4·7. *A substance weighing 27* g *and at 100°C was dropped into a Bunsen's ice calorimeter and the liquid column in the capillary tube recedes through a distance of 10* cm. *Calculate the specific heat of the substance. Area of cross-section of the tube = 3* sq mm.

Here $M = 27\ \text{g},\ S = ?,\ \theta = 100^\circ\text{C}$

$l = 10\ \text{cm},$

$$a = 3\ \text{sq mm} = \frac{3}{100}\ \text{sq cm}$$

$$\therefore \quad v = l \times a = 10 \times \frac{3}{100} = \frac{3}{10}\ \text{cc}$$

$$MS\theta = \frac{80\,v}{0\cdot 09}$$

$$27 \times S \times 100 = \frac{80 \times 3}{10 \times 0\cdot 09}$$

$$S = \mathbf{0\cdot 098\ cal/g\text{-}^\circ C}$$

4·16 Cooling Effect due to Vaporization

If a person pours a little spirit on his hand, he feels a cooling effect. The spirit evaporates and takes latent heat of vaporization from the spirit left behind and the hand. Due to this reason one feels a cooling effect

Thus, whenever evaporation of a liquid takes place, the remaining liquid shows a fall in temperature.

The molecules of a liquid are always in a state of random motion. They collide with each other and they may or may not change their respective kinetic energies. Due to the collision a certain molecule may acquire more energy than the energy with which it is held. As soon as this happens the molecule flies off, *i.e.*, it leaves the liquid surface. This is called evaporation. If no external heat is supplied it is obvious that the mean kinetic energy of the molecules decreases and the temperature of the liquid falls. This explains cooling caused by evaporation. If the moving vapour molecules come near to each other at sufficiently low velocities, they experience a greater magnitude of force of attraction. The molecules coalesce and this results in condensation. Rate of evaporation increases with increase in temperature of the liquid and decrease in pressure over the liquid surface.

4·17 Cryophorus

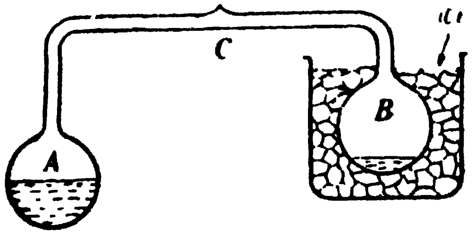


Fig. 4·8.

A cryophorus consists of two glass bulbs *A* and *B* connected through a glass tubing *C* (Fig. 4·8). The bulb *A* contains water.

Air in *B* and the tube is removed with an evacuation pump and the tube is sealed. The space inside *B* and the tube contains water vapour only. The vessel *B* is surrounded by freezing mixtures. Water vapour in *B* condenses and the pressure over the surface of water in *A* falls. Evaporation of water takes place. The process continues at a rapid rate and the temperature of water in *A* decreases. After some time water in *A* begins to freeze.

To prevent any heat from the surroundings to flow into *A*, it is covered with a non-conducting material like cotton or flannel.

4·18 Examples of Cooling Caused by Evaporation

1. In hot weather, we perspire. Water from the body comes out of the fine pores of the skin. Water evaporates and takes heat of vaporization from the body. Due to this reason we feel a cooling sensation.

2. A person wearing wet clothes feels chill. Water evaporates taking the latent heat of vaporization from the body and the person feels chill.

3. Water in an earthen pot remains cool in summer. Water comes out of the pores of the vessel and evaporates. During evaporation, the latent heat is taken from the remaining water. Therefore water remains cool in an earthen vessel.

4. Streets, floors, gardens, lawns etc. are watered in summer. Water evaporates taking the latent heat from them and keeps them cool.

5. Dogs keep their tongues usually out in summer. Water evaporates from the tongue and keeps it cool.

6. *Khas-khas* screens are commonly used in summer. Water is poured on them. Water evaporates and takes heat from them and the air in the room. Due to this reason the room is kept cool.

7. During high fever, a wet cloth soaked in 'Eau de cologne' or ice cold water is kept on the forehead. The liquid evaporates rapidly and takes heat from the head and the body.

8. Hot liquids are poured in a plate to increase the surface area. The rate of evaporation increases and the liquid cools quickly.

9. When a wet muslin piece is wrapped around the bulb of a thermometer, the thermometer records fall of temperature. Water evaporates and takes latent heat from mercury in the bulb.

10. In a packed hall in summer a person feels uneasy. Perspiration from his body does not evapbrate. As soon as he comes out of the hall he feels a sudden cooling sensation. Perspiration evaporates rapidly and takes heat from his body.

4 19 Refrigeration

The second law of thermodynamics as given by Clausius gives the principle of working of a refrigerator and ice plants.

"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance."

This part is applicable in the case of ice plants and refrigerators. Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature But, it is possible, if some external work is done on the working substance. Take the case of an ammonia ice plant. Ammonia is the working substance. Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted into low pressure vapour. External work is done to compress the ammonia vapour to high pressure. This ammonia at high pressure is passed through coils over which water at room temperature is poured Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature). This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia. If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

4·20 Ammonia Ice Plant

Ammonia ice plant is commonly used to manufacture ice. It is based on the principle that evaporation causes cooling. Moreover in this plant, heat flows from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance The schematic sketch of an ammonia ice plant is shown in Fig. 4·9.

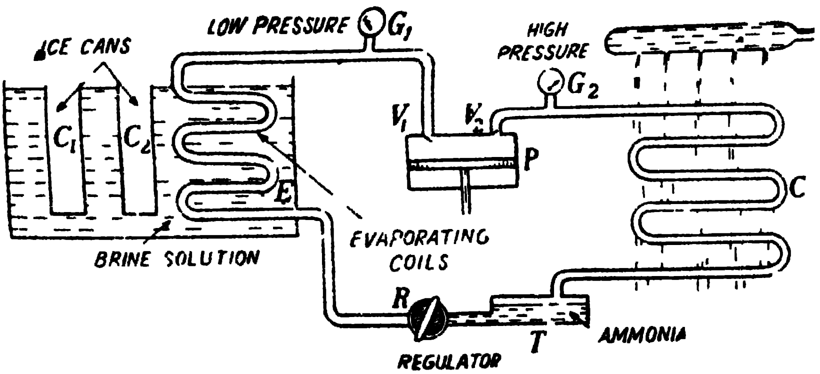


Fig. 4 9

(1) T is a reservoir containing ammonia liquid.

(2) R is a regulator called the expansion valve or throttle valve. High pressure liquid expands towards the low pressure side and with the fall in pressure there is a fall in saturation temperature. Liquid ammonia at low temperature and pressure entering the coils evaporates and takes heat from the surrounding brine solution.

(3) The brine tank contains ice cans C_1 and C_2 containing pure water.

(4) The compression pump P is worked with the help of an electric motor. It has two valves V_1 and V_2. When the piston is moved outwards, valve V_1 opens and V_2 is closed. Ammonia vapour enters the cylinder. When the piston is moved inwards, V_1 closes and V_2 opens. Compressed ammonia vapour is passed through the condensing coils C.

(5) G_1 is the low pressure gauge and G_2 is the high pressure gauge. When the pump works, the rate of evaporation of ammonia liquid in the evaporating coils increases and the temperature of the brine solution gradually falls.

(6) The compressed ammonia vapours passing the condensing coils give heat to water falling over the coils. Ammonia vapours get condensed and liquid ammonia is formed. The liquid ammonia enters the reservoir.

The cycle of operations is repeated and the temperature of brine solution in the tank decreases to - 8°C. Water in the cans freezes to ice.

(i) If the pump stops working, then the cyclic process does not take place and the temperature of the brine tank does not fall.

(ii) The function of electricity is to move the piston to and fro with the help of the electric motor and to compress the vapours.

(iii) Ammonia is the working substance. It takes heat from the brine solution (at low temperature) and transfers heat to the water falling on the condensing coils at the room temperature. *It means heat is transferred from a body at a lower temperature to a body at a higher temperature.* Ordinarily it is not possible. But by doing *external work (with the help of the pump) on the working substance* this transfer of heat is possible and this is in accordance with the second law of thermodynamics.

4·21 Solid Carbon Dioxide—(Dry Ice)

A cylinder containing liquid CO_2 is taken. A muslin bag is tied to the nozzle. The cylinder is placed in a slanting position (Fig. 4·10). The valve *V* is opened and the liquid CO_2 enters the muslin bag. The liquid CO_2 evaporates rapidly and takes the latent heat of vaporization from the remaining liquid in the bag. Liquid CO_2 solidifies and solid CO_2 is formed in the muslin bag

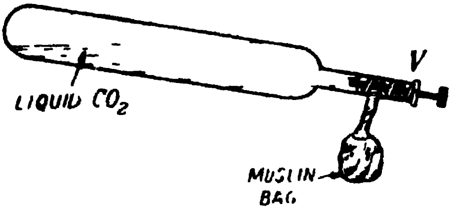


Fig. 4·10

The temperature of solid CO_2 is —78°C and it is also called *dry ice.* It is commonly used by doctors for dressing the wounds. It serves as refrigerant when mixed with ether. Solid CO_2 does not melt when exposed to air. It directly evaporates and forms its vapours.

4·22 Gas and Vapour

Gas and vapour states are the two distant stages of the same continuous phenomenon. These two states have distinct boundary which is governed by a particular temperature called the critical temperature. Above the critical temperature the substance is in the gaseous state and below the critical temperature it is in the vapour state.

A gas cannot be liquefied by mere application of pressure, howsoever high the pressure may be A vapour can be liquefied by applying pressure. Therefore to liquefy a gas, first it has to be cooled to a temperature lower than its critical temperature It means it is converted from a gaseous state to the vapour state. Then a high pressure is applied and the vapours get liquefied.

Critical temperature of a gas is that temperature above which the gas cannot be liquefied by mere application of pressure, howsoever large the pressure may be.

TABLE

Critical Temperature

Substance	*Critical temperature °C*
Water	374
Ammonia	132
Carbon dioxide	31
Oxygen	—119
Hydrogen	—240
Helium	—268

4·23 Saturated and Unsaturated Vapours

Take three clean barometer tubes *A*, *B* and *C* as shown in Fig. 4·11. The level of mercury in each tube is up to the same height. The space above mercury in all the tubes is Torricellian vacuum.

With the help of a bent pipette introduce water into the tube *B*. Water rises to the top and evaporates. Level of mercury in the tube *B* falls. The space above mercury in *B* contains water vapours. There is no water left on the surface of mercury. These vapours are unsaturated and the pressure exerted by the vapours is *h*.

Similarly continue introducing water in the tube *C*. The level of mercury gradually falls. A stage is reached when no more water introduced in the tube *C* evaporaters (Fig. 4·11). It means the space above mercury in *C* is completely saturated with water vapours. It cannot contain more vapours. The difference in the levels of mercury in *A* and *C* is *H* and it represents the saturated vapour pressure of water at the room temperature.

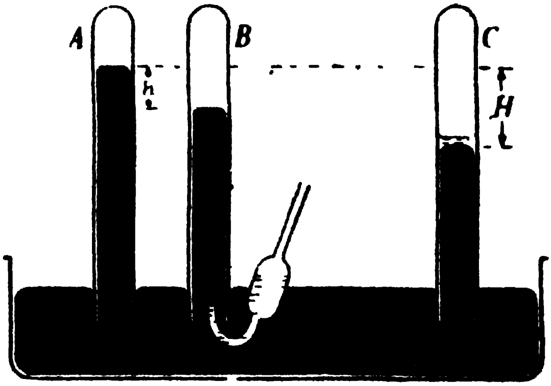


Fig. 4·11

A space is said to be saturated with water vapours if it cannot contain more vapours It is unsaturated if it can contain more vapours.

(1) The saturated vapour pressure of a liquid depends on its temperature. The saturated vapour pressure increases with rise in temperature and decreases with fall in temperature.

(2) The saturated vapour pressure depends on the nature of the substance.

(3) The saturated vapour pressure does not depend on the volume occupied by the vapours.

(4) The saturated vapour of a liquid is independent of the presence of the vapours of other liquids present. The vapours should not have any chemical action.

(5) The total pressure exerted by the vapours of all substances is equal to the sum of the pressures exerted by the vapours of individual substances,

$$P = P_1+P_2+P_3+\ldots$$

(6) The saturated vapours do not obey the gas laws whereas unsaturated vapours obey the gas laws.

In Fig. 4·12, the curve *AB* shows that with decrease in volume the pressure increases. From *A* to *B* the vapour is unsaturated and obeys Boyle's law.

At *B* the vapour is saturated and exerts maximum pressure. With decrease in volume beyond, *B*, the pressure is constant. From *B* to *C* it represents the change from the saturated vapour to the liquid state.

If the temperature of a saturated vapour is gradually increased the pressure increases From *A* to *B* the vapour is saturated (Fig. 4·13). Beyond *B* if the temperature is increased, the vapour is unsaturated and pressure increases with temperature. In the region *BC*, the pressure of the unsaturated vapour is directly proportional to its absolute temperature.

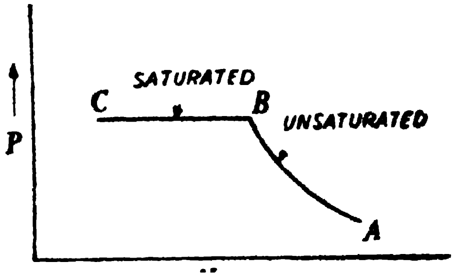


Fig. 4·12

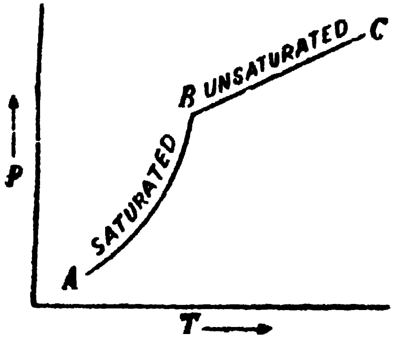


Fig. 4·13

4·24 Vapour Pressure of Liquids

The vapour pressure of a liquid is dependent only on its temperature. The vapour pressure, in general, increases with rise in temperature. The normal boiling point is that temperature at which the vapour pressure of the substance is equal to the normal pressure *i.e.* 76 cm of Hg. If the atmospheric pressure is lower or higher than the normal pressure, the liquid will boil at a temperature lower or higher than the normal boiling point. Usually the atmospheric pressure in Delhi is less than 76 cm of Hg and water boils at a temperature lower than 100°C. For the measurement of vapour pressure the apparatus shown in Fig. 4·14 is used.

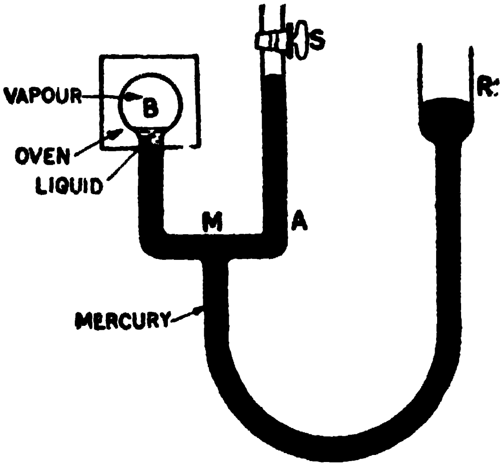


Fig. 4·14

The bulb B contains the vapour in contact with its liquid. M is a manometer limb and R is a reservoir containing mercury. At high temperatures, the stop-cock S is kept open and the tube is filled with a gas at high pressure. Adjust the reservoir R such that the liquid appears in the tube inside the oven. If the pressure of the gas in the limb A is P_0 and the difference in levels of mercury in the manometer limbs is h, then vapour pressure of the liquid at the temperature T is given by

$$P = P_0 + h \qquad \ldots(i)$$

In this way the vapour pressure of the liquid at any temperature can be determined.

For low vapour pressure measurement (*i.e.*, at low temperatures) the reservoir R is raised so that the level of mercury in the limb A is above the stop-cock S. The stop-cock S is closed The vessel B is surrounded by the low temperature bath and the reservoir R is adjusted so that the liquid in the tube is within the bath. The difference in the levels of mercury in the manometer directly measures the vapour pressure. In this case $P_0 = 0$

$$\therefore \qquad P = h \qquad \ldots(ii)$$

As the temperature of the liquid is lowered, a state is reached when the liquid begins to solidify. The temperature and pressure correspond to the *triple point*. At the triple point the substance exists as a solid, liquid and vapour simultaneously.

4·25 Triple Point

(*i*) The melting point of ice decreases with increase in pressure. It means that ice melts at a temperature lower than 0°C at a pressure higher than the normal pressure. The curve AB (Fig. 4·15) represents the relation between pressure and temperature. The curve AB is called the ice line The substance will exist in the solid state (ice) to the left of the curve AB and in the liquid state to the right of the curve AB. The curve AB represents the equilibrium between the liquid and the solid states.

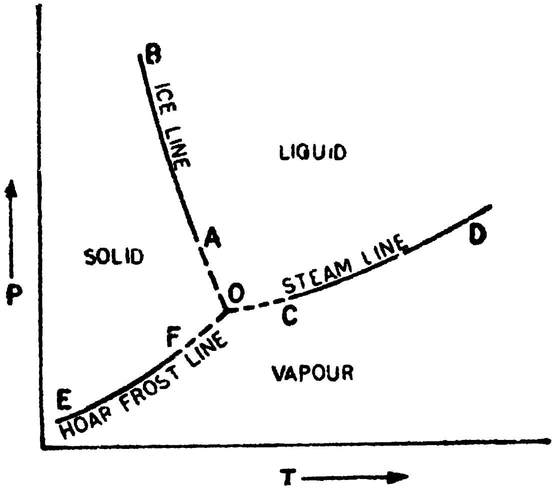


Fig. 4·15

(*ii*) The boiling point of water increases with increase in pressure. The curve OD represents the relation between pressure and temperature and it is called the steam line. Above the curve OD, the substance is in the liquid state and below the curve *CD* it is in the vapour state. The curve *CD* represents the equlibrium between the liquid and the vapour states.

(*iii*) The curve *EF* represents equilibrium between the solid and the vapour states of a substance and is called the ***Hoar Frost*** line. Above the curve *EF*, the substance is in the solid state and below the curve *EF* it is in the vapour state.

These three curves should meet at a point *O* as shown in Fig. 4·15. Suppose these curves do not meet at a point as shown in Fig. 4·16 and they enclose an area *ACF*. It means, according to the ice line, the substance must be only in the solid state in the shaded portion. According to the steam line, the substance must be only in the liquid state and according to the hoar frost line the substance must be only in the vapour state. Thus in the shaded portion, the substance must exist simultaneously in the solid, liquid and the vapour states. It is not possible. Therefore, the three curves must meet at a single point *O*, called the triple point.

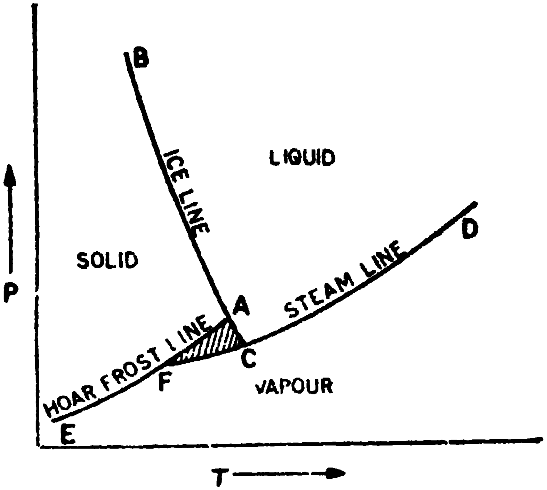


Fig. 4·16

For water, the temperature and pressure corresponding to the triple point are 0·0075°C and 4·58 mm of Hg respectively. The triple point of water is not fixed but is different for different *allotropic forms of ice.*

Triple Points

	T (K)	*Pressure (mm of Hg)*
H_2	13·84	52·8
N_2	63 18	94·0
O_2	54 36	1·14
CO_2	216 65	3·880
H_2O	273·1675	4·58
I	387	90·0

4·26 Gibbs' Phase Rule

Gibbs' phase rule represents the condition of equilibrium between the number of coexisting phases and the components.

Consider a heterogeneous system consisting of P phases and containing C components in equilibrium. Let the different phases be represented by the superscripts $a, b, c \dots p$ and let the components be represented by the subscripts 1, 2, 3,...C. The concentration of any of the components in the different phases may be different. The system is assumed to be in mechanical and thermal equilibrium. This means that all the phases are at the same temperature and pressure. It is further assumed that there is no chemical reaction between the components in the system.

Let the chemical potentials of the different components in the P-phases be written as

$$\begin{array}{lll}
\mu_1^a, \ \mu_2^a, \dots & & \dots \mu_C^a \\
\mu_1^b, \ \mu_2^b, \dots & & \dots \mu_C^b \\
\dots & \dots & \dots \\
\dots & \dots & \dots \\
\mu_1^p, \ \mu_2^p, \dots & & \dots \mu_C^p
\end{array}$$

Now consider that small amounts (dn) of the components are transferred under equilibrium conditions, from one phase to another. It follows that

$$\left.\begin{array}{llll}
dn_1^a + dn_1^b + dn_1^c \dots & & \dots dn_1^p & = 0 \\
dn_2^a + dn_2^b + dn_2^c \dots & & \dots dn_2^p & = 0 \\
\dots \quad \dots & \dots & & \dots \\
\dots \quad \dots & \dots & & \dots \\
dn_C^a + dn_C^b + dn_C^c \dots & & \dots dn_C^p & = 0
\end{array}\right\} \quad \dots(i)$$

From Gibbs-Duhem relation, at equilibrium, the change in Gibbs' potential

$$\left.\begin{array}{rl}
 & dG = \Sigma\mu \, dn = 0 \\
\therefore \quad \Sigma\mu \, dn = & (\mu_1^a dn_1^a + \mu_1^b dn_1^b + \dots \quad \dots \mu_1^p dn_1^p) \\
 & + (\mu_2^a dn_2^a + \mu_2^b dn_2^b + \dots \quad \dots \mu_2^p dn_2^p) \\
 & \dots \quad \dots \quad \dots \quad \dots \\
 & \dots \quad \dots \quad \dots \quad \dots \\
 & + (\mu_C^a dn_C^a + \mu_C^b dn_C^b + \dots \mu_C^p dn_C^p) = 0
\end{array}\right\} \dots(ii)$$

Multiplying the set of equations in (i) by C different multipliers,

$$\left.\begin{array}{llll}
\lambda_1, \lambda_2 \dots \quad \dots \lambda_C, & & & \\
\lambda_1 dn_1^a + \lambda_1 dn_1^b + & \dots + \lambda_1 dn_1^p & = 0 & \\
\lambda_2 dn_2^a + \lambda_2 dn_2^b + & \dots + \lambda_2 dn_2^p & = 0 & \\
\dots \quad \dots & \dots & \dots & \\
\dots \quad \dots & \dots & \dots & \\
\lambda_C dn_C^a + \lambda_C dn_C^b + & \dots \lambda_C dn_C^p & = 0 &
\end{array}\right\} \quad \dots(iii)$$

Adding equations (*ii*) and (*iii*) and equating the coefficients of dn terms to zero, we get

$$\left.\begin{array}{l} -\lambda_1 = \mu_1{}^b = \mu_1{}^b = \ldots \quad \ldots = \mu_1{}^p \\ -\lambda_2 = \mu_2{}^a = \mu_2{}^b = \ldots \quad \ldots = \mu_2{}^p \\ \ldots \qquad \ldots \qquad \ldots \\ \ldots \qquad \ldots \qquad \ldots \\ -\lambda_C = \mu_C{}^a = \mu_C{}^b = \ldots \quad \ldots = \mu_c{}^p \end{array}\right\} \qquad (iv)$$

The set of equations in (*iv*) are the equations of phase equilibrium It means that at equilibrium, the chemical potentials of a component in all its phases must be equal. However chemical potentials are different for different components.

In every phase there are C different components having C different concentrations. But for a closed system if concentrations of $(C-1)$ components are arbitrarily chosen, the concentration of the last component is automatically fixed. Therefore, there are $(C-1)$ composition variables in each phase For P phases the number of composition variables would be

$$P(C-1)$$

In addition to this value, there are two other variables *viz*, pressure and temperature. Thus the total number of variables will be,

$$= P(C-1)+2 \qquad \ldots(v)$$

Further it has been shown that if chemical potential of any one of the P phases is defined then the chemical potential of the remaining $(P-1)$ phases is fixed. Therefore for C components the invariant composition variables will be

$$= C(P-1) \qquad \ldots(vi)$$

Therefore the number of independent variables of a system will be given by

$$F = P(C-1)+2-C(P-1) \qquad \ldots(vii)$$

Here F represents the number of degrees of freedom.

From equation (*vii*)

$$F = C-P+2 \qquad \ldots(viii)$$

or

$$P+F = C+2 \qquad \ldots(ix)$$

Water can exist in three states, *viz.*, solid, liquid and vapour. These are called the three phases of water. A component is defined as a distinct chemical substance different from others Ice, water and steam refer to the same component *viz.*, water.

In Fig. 4·15, above the curve *CD*, water exists only in the liquid state In the space *BOD*, the pressure or temperature can be changed independently without any change in the phase of a substance. Thus a substance has two degrees of freedom (temperature and pressure) and only one phase (liquid).

Along the curve *OD*, the substance has two phases (liquid and vapour) but only one degree of freedom (temperature or pressure).

If the pressure is changed the temperature also changes along the curve OD.

At the triple point the substance has three phases (solid, liquid and vapour) and no degree of freedom.

According to Gibbs' phase rule, the sum of the number of phases and the number of degrees of freedom is equal to the number of components plus two.

Let P represent the number of phases, F the number of degrees of freedom and C the number of components. Then

$$P+F = C+2$$

(*i*) For the liquid state, (region BOD)

$$P = 1, F = 2 \text{ and } C = 1$$

$$1+2 = 1+2$$

(*ii*) For the liquid-vapour state (curve OD)

$$P = 2, F = 1, C = 1$$

$$2+1 = 1+2$$

(*iii*) For the solid-liquid-vapour state (triple point)

$$P = 3, F = 0, C = 1$$

$$3+0 = 1+2$$

The phase rule has practical applications when the components involved are more than one, *e.g.*, freezing mixtures (ice and salt).

4·27. Hygrometry

It is that branch of physics which deals with the study of water vapour in the atmosphere.

Relative humidity. It is defined as the ratio of the mass of water vapour (m) actually present in a certain volume of air at room temperature to the mass of water vapour (M) required to saturate the same volume of air at the same temperature.

$$\text{R.H.} = \frac{m}{M}$$

Also R.H. $= \frac{p}{P}$ where p is the actual vapour pressure and P is the saturated vapour pressure at room temperature.

Dew point. It is the temperature at which the water vapour actually present in the atmosphere is just sufficient to saturate it. It means that the actual vapour pressure at room temperature is equal to the saturated vapour pressure at dew point.

Absolute humidity. It is the amount of water vapour actually present in one cubic metre volume of atmospheric air.

4 28 Deniell's Hygrometer

Daniell's hygrometer consists of two glass bulbs A and B connected by a glass tubing and the space inside is evacuated and sealed (Fig 4·17). The bulb A contains an evaporating liquid and the space above it, its vapour. The thermometer T_1 fixed on the stand measures the room temperature and the thermometer T_2 fixed inside the glass tubing dips in the liquid of bulb A and measures the dew point temperature.

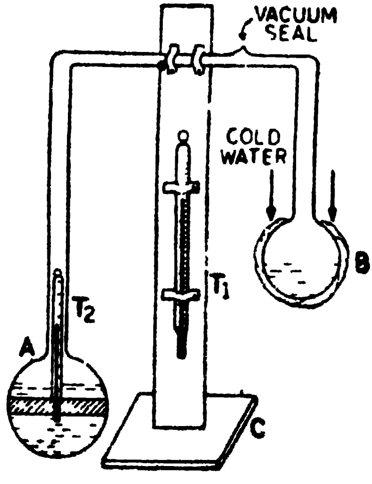


Fig. 4·17

A piece of cotton is tied around B and ether is poured over it. The vapours inside the bulb B condense, some vacuum space is created and the liquid evaporates and this causes cooling of the liquid in the bulb A. When the temperature of the bulb A reaches the dew point, the water vapours present in the atmospheric air condense on the bright metallic ring and it becomes dim. By continuously pouring ether on the bulb B, the temperatures at which dew just appears and disappears are noted and the mean temperature measures the dew point temperature.

From the standard tables the saturated vapour pressures at dew point and room temperature are noted and the relative humidity is calculated

$$RH = \frac{\text{Saturated vapour pressure at dew point } (T_2)}{\text{Saturated vapour pressure at room temp.} (T_1)}$$

$$\% RH = \left(\frac{\text{Saturated vapour pressure at dew point } (T_2)}{\text{Saturated vapour pressure at room temp. } (T_1)}\right) \times 100$$

4 29 Regnault's Hygrometer

Regnault's hygrometer consists of two glass tubes A and B in which two thermometers T_1 and T_2 are fixed (Fig. 4·18). C_1 and C_2 are two bright silver caps fixed at the bottom of the glass tubes. One of the test tubes say A containing a volatile liquid (ether) is connected to an aspirator and when water is drawn from the aspirator an equal amount of atmospheric air bubbles through the liquid in A and this causes evaporation of the liquid. The temperature of A goes down and when it reaches the dew point temperature dew appears on the metallic cap C_1 and the cap becomes dim. With the help of a telescope kept at a distance, the temperatures at which dew appears and disappears are noted and the mean of these two temperatures measures the dew point. The thermometer T_1 measures the room temperature.

From the standard tables. the saturated vapour pressures of water vapour corresponding to the room temperature and the dew point temperature are noted and relative humidity is calculated.

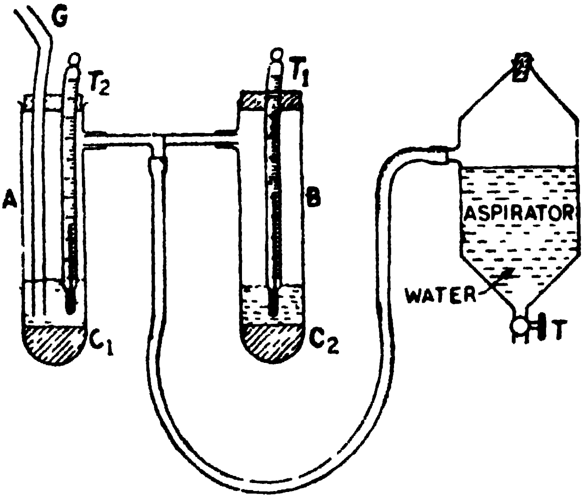


Fig. 4·18

$$\%RH = \left[\frac{\text{Saturated vapour pressure at dew point}}{\text{Saturated vapour pressure at room temp.}}\right]\times 100$$

Advantages of Regnault's hygrometer over Daniell's hygrometer. (1) In the Regnault's hygrometer, the rate of cooling is controlled and is quicker as compared to the Daniell's hygrometer.

(2) In the Regnault's hygrometer, the air bubbling through the whole mass of ether keeps the same temperature throughout the liquid whereas in a Daniell's hygrometer the temperature at the surface of the liquid is less than the interior of the liquid.

(3) Due to the silver caps at the bottom of the tubes in Regnault's hygrometer, temperatures inside and outside are the same. In the Daniell's hygrometer the metal ring is not in direct contact with the liquid due to the glass bulb.

(4) In Regnault's hygrometer, ether is not wasted as in the case of Daniell's hygrometer.

(5) In the case of Regnault's hygrometer, observations are taken at a distance with the help of telescope. Therefore, the breath of the observer and the heat of the body do not affect the humidity. It is not so in the case of the Daniell's hygrometer.

(6) Due to silver caps, the moment when the dew just appears or disappears can be noted very accurately in the case of the Regnault's hygrometer. But it is not so in the case of the Daniell's hygrometer.

4·30 Wet and Dry Bulb Hygrometer

Take two half degree centigrade thermometers. See that both show the same temperature when immersed in water. If they differ, change one of them. Take a piece of clean muslin cloth or wash the muslin cloth with soap. Remove any grease from the muslin piece. Finally wash the piece with clean water. Tie one end of the muslin piece to the bulb of one of the thermometers. Suspend the thermometers from the iron rod of the retort stand (Fig 4·19).

Adjust the height of the iron stand, so that one end of the muslin piece dips in water. The bulb of the thermometer should not dip in water. Water will rise through the muslin piece and will evaporate. Note the temperature of the dry bulb thermometer. Also record the temperature of the wet bulb thermometer (thermometer having muslin piece) after every one minute. Do not place the apparatus near an open window or under a fan. When the wet bulb thermometer shows a constant temperature, record it. Also note the temperature of the dry bulb thermometer after the experiment. Calculate *RH* and dew point with the help of constant tables.

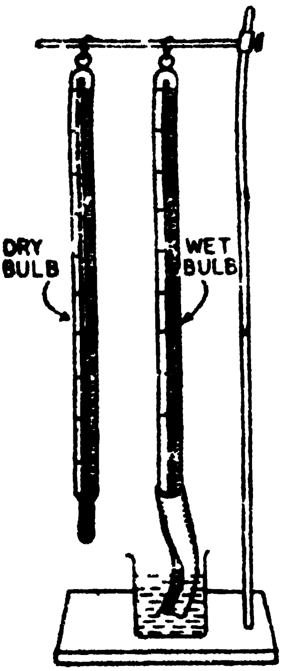


Fig 4·19

Relative humidity is defined as the ratio of the actual vapour pressure at room temperature to the saturated vapour pressure at room temperature.

$$RH = \frac{\text{Actual } VP \text{ at room temperature}}{SVP \text{ at room temprerature}}$$

Dew point is defined as that temperature at which water vapours actually present in the atmosphere are just sufficient to saturate it. The actual vapour pressure at room temperature is equal to the saturated vapour at dew point. Therefore,

$$RH = \frac{\text{Saturated } VP \text{ at dew point}}{\text{Saturated } VP \text{ at room temperature}}$$

Suppose, dry bulb reading before the experiment

$= t_1°\text{C} = \ldots$

Dry bulb reading after the experiment

$= t_2°\text{C} = \ldots$

Mean dry bulb reading $= \left(\frac{t_1+t_2}{2}\right)°\text{C} = \ldots$

No.	*Wet bulb reading*
1	...
2	...
...	
...	
...	
...	
...	
20	...

Calculations. Dry bulb reading $A = ...$

Wet bulb reading

(Constant reading at the end) $B = ...$

Difference between the dry and wet bulb readings

$$= (A-B) = ...$$

From wet and dry bulb humidity tables :

Saturated vapour pressure [Note the reading for dry bulb temperature (A) under zero column]

$$P = ...$$

Actual vapour pressure [Note the reading for wet bulb temperature (B) under difference column for (A—B)]

$$= p = ...$$

$$\%RH = \frac{p}{P} \times 100$$

Dew point (Find the value in the zero column for the value of p, and find the corresponding temperature)

$$= ......°C$$

WET AND DRY BULB HUMIDITY TABLE

Temperatures in °C and Saturation Pressures
in mm of mercury

Reading in °C Wet bulb	*Difference between dry and wet bulb in °C*											
	0°	1°	2°	3°	4°	5°	6°	7°	8°	10°	12°	14°
0	4·6	4·1	3·6	3·1	2·6	2·1	1·6	1·1	0·6			
2	5·3	4·8	4·3	3·8	3·3	2·8	2·3	1·8	1·3			
4	6·1	5·6	5·1	4·6	4·1	3·6	3·1	2·6	2·1			
6	7·0	6·5	6·0	5·5	5·3	4·5	4·0	3·5	3·0	2·0		
8	8·0	7·5	7·0	6·5	6·0	5·5	5·0	4·5	4·0	3·0		
10	9·2	8·7	8·2	7·7	7·2	6·7	6·2	5·7	5·2	4·1		
11	9·8	9·3	8·8	8·3	7·8	7·3	6·8	6·3	5·8	4·8	3·8	2·7
12	10·5	10·0	9·5	9·0	8·5	8·0	7·5	7·0	6·5	5·4	4·4	3·4
13	11·2	10·7	10·2	9·7	9·2	8·7	8·2	7·7	7·2	6·1	5·1	4·1
14	12·0	11·5	11·0	10·5	10·0	9·4	8·9	8·4	7·9	6·9	5·9	4·9
15	12·8	12·3	11·8	11·3	10·8	10·2	9·7	9·2	8·7	7·7	6·7	5·7
16	13.6	13.1	12·6	12·1	11·6	11·1	10·6	10·1	9·5	8·5	7·1	6·5
17	14·5	14·0	13·5	13·0	12·5	12·0	11·5	11·0	10·5	9·5	8·4	7·4
18	15·5	15·0	14·5	13·9	13·4	12·9	12·4	11·9	11·4	10·4	9·3	8·3
19	16·5	16.0	15·5	14·9	14·4	13·9	13·4	12·9	12·4	11·4	10·3	9·3
20	17·6	17·1	16·5	16·0	15·5	15·0	14·5	13·9	13·4	12·4	14·4	10·3
21	18·7	18·1	17·6	17·1	16·6	16·1	15·6	15·1	14·6	13·5	12·5	11·5
22	19·8	19·3	18·8	18·3	17·8	17·3	16·8	16·2	15·7	14·7	13·7	12·6
23	21·0	20·6	20·1	19·5	19·0	18·5	18·0	17·5	17·0	15·9	14·9	13·9
24	22·4	21·9	21·4	20·8	20·3	19·8	19·3	18·8	18·3	17·2	16·2	15·2
25	23·8	23·3	22·8	22·3	21·7	21·2	20·7	20·2	19·7	18·6	18·6	16·6
26	25·2	24·7	24·2	23·7	23·2	22·6	22.1	21·6	21·1	21·0	19·0	18·0
27	26·8	26·2	25·7	25·2	24·7	24·2	23·7	23·1	22·6	21·6	20·6	19·5
28	28·4	27·8	27·3	26·8	26·3	25·8	25·3	24·7	24·2	23·2	22·2	21·1
29	30·1	29.8	29.0	28·5	28·0	27·5	27·0	26·4	25·9	24·9	23·9	22·8
30	31·9	31·3	30·8	30·3	29·8	29·3	28·8	28·2	27·7	26·7	25·6	24·6
32	35·7	35·2	34·7	34·1	33·6	33·1	33·6	32·0	31·5	30·5	29·5	28·4
34	39·9	39·4	38·9	38·4	37·9	37·3	36·8	36·3	34·8	34·7	33·7	32·7
36	44·6	44·1	43·6	43·0	42·5	42·0	41·5	40·9	40·4	39·4	38·4	37·3
38	49·7	49·2	48·7	48·2	47·7	47·1	46·6	46·1	45·6	44·5	43·5	42·4
40	55·4	54·9	54·4	53·9	53·8	52·8	52·3	51·7	51·2	50·2	49·1	48·1

4·31 Weather

Dew, rain, clouds, fog, mist, hails, snow, hoar frost etc. are due to the condensation of water vapours present under different conditions in the atmosphere.

Dew. Dew is formed on grass and leaves in the early hours of the morning. The temperature of the atmosphere during the night gradually falls. In the early morning if the temperature of the atmosphere is less than the dew point temperature, formation of dew takes place. The saturated vapours when they come in contact with grass or leaves condense in the form of fine drops of water.

If the night is cloudy, the temperature of the earth does not fall and dew is not formed. A clear sky free from wind is helpful in the formation of dew.

Hoar Frost. If the temperature of the atmosphere falls below 0°C, the dew formed on the leaves and grass freezes and it is called hoar frost.

Fog and Mist. When water vapours present in the atmosphere condense on dust particles in the atmosphere, fog is formed. There is no basic difference between fog and mist. Thick mist is called fog. A clear cold night is favourable for the formation of fog and mist.

Clouds and Rain. When the fog is formed at high altitudes it is called a cloud. When small drops of water in the cloud combine together, bigger water drops are formed and fall in the form of rain.

Snow and Hail. When the cloud suddenly passes through a very cold region the water drops freeze and fall in the form of snow and hail. Snowfall is common in hill stations because of very low temperature in winter. Hails are caused due to the freezing of rain drops in the atmosphere. Hails are hard and of different sizes whereas snow is quite soft.

Example 4·1. *If the temperature of air is 16·5°C and dew point is 6·5°C, find the % relative humidity of air.*

S.V.P. at 6°, 7°, 16° and 17° are 7·05, 7·51, 13·62 and 14·42 mm *respectively.*

$$\text{Dew point} = 6{\cdot}5^\circ\text{C}$$

$$\text{Room temperature} = 16{\cdot}5^\circ\text{C}$$

$$S.V.P. \text{ at } 6{\cdot}5^\circ\text{C} = \frac{S.V.P. \text{ at } 6^\circ + S.V.P. \text{ at } 7^\circ}{2}$$

$$p = \frac{7{\cdot}05+7{\cdot}51}{2} = 7.28 \text{ mm}$$

$$S.V.P. \text{ at } 165^\circ\text{C} = \frac{S.V.P. \text{ at } 16 + S.V.P. \text{ at } 17}{2}$$

$$P = \frac{13{\cdot}62+14{\cdot}42}{2} = 14{\cdot}02 \text{ mm}$$

$$R.H. = \frac{p}{P} \times 1000$$

$$= \frac{7{\cdot}28}{14{\cdot}02} \times 100 = \mathbf{51{\cdot}9\%}$$

Example 4·2. *Calculate the dew point when the relative humidity of air at 20°C, is 52%. Given the S.V.P. of water at 20°C, 10°C and 9°C are 17·5, 9·2, 8·6* mm *of* Hg *respectively.*

(Punjab 1966)

$$R.H. = \frac{S.V.P. \text{ at dew point}}{S.V.P. \text{ at room temperature}} = \frac{p}{P}$$

$$0{\cdot}52 = \frac{p}{17{\cdot}5}$$

$$p = 9{\cdot}1 \text{ mm}$$

For 1°C difference $= 9{\cdot}2 - 8{\cdot}6 = 0{\cdot}6$ mm

∴ Dew point temperature

$$= 9 + \frac{0{\cdot}5}{0{\cdot}6} = \mathbf{9{\cdot}83°C}$$

Exercises IV

1. What do you understand by change of state ?

2. What is triple point ? Show that the steam line, the ice line and the Hoar frost line meet at a single point.

3. Discuss Gibbs' phase rule. What do you understand by phase, degree of freedom and component ?

4. Define hygrometry, relative humidity, dew point and absolute humidity.

5. Describe the construction and working of a Daniell's hygrometer.

6. Describe the construction and working of a Regnault's hygrometer. How is it used to determine the relative humidity ? Compare it with a Daniell's hygrometer.

7. What is the difference between a gas and a vapour ?

8. Distinguish between saturated and unsaturated vapours.

9. What do you understand by relative humidity and dew point ?

10. Describe briefly a wet and a dry bulb hygrometer.

11. Explain briefly the following .

(*i*) Dew (*ii*) Hoar frost (*iii*) Fog (*iv*) Mist (*v*) Clouds (*vi*) Snow (*vii*) Hail (*viii*) Rain.

12 Derive Gibbs' phase rule and discuss the equilibrium of a saturated solution and the solid of the dissolved substance.

[Delhi (Hons) 1976]

13. On a certain day the *RH* is 66·67%. The saturated vapour pressure at room temperature is 18·6 mm. Calculate the saturated vapour pressure at dew point. [**Ans.** 12·4 mm]

14. On a certain day the dew point is 18 6°C and the room temperature is 23·7°C. The saturated vapour pressures of water at 18°C, 19°C, 23°C, and 24°C are 15·46 mm, 16·46 mm, 21·02 mm and 22 32 mm of Hg respectively. Calculate the relative humidity. [**Ans.** 73·23%]

15. On a certain day the dew pont is 8 5°C and the room temperature is 18·4°C. Find the *RH* if maximum vapour pressure for 8°C, 9°C, 18°C, and 19°C are 8 04, 8·61, 15 46 and 16 46 mm of mercury column respectively. [**Ans.** 52·5%]

16. Find the result of mixing 10 g of ice at −10°C with 10 g of water at 10°C. Sp heat of ice = 0·5 and latent heat of ice = 80 cal/g. [**Ans.** A mixture of 9·375 g of ice and 10·625 g of water at 0°C)

17. What will be the result of mixing 400 g of copper chips at 500°C with 500 g of melting ice ? [**Ans.** 250 g of ice melts. Final temperature = 0°C]

18. The density of ice is 0·93 g/cc at 0°C. A piece of metal weighing 1·50 g is heated to 100°C and is then placed in a Bunsen's ice calorimeter. The decrease in volume is found to be 1 876 cc. Calculate the specific heat of the metal Latent heat of ice = 80 cal/g. [**Ans.** 0·133 cal/g-°C]

19. A solid of mass 20 g is heated to a temperature of 80°C and quickly dropped in a Bunsen's ice calorimeter. The contraction in volume observed is 0·9 cc. The contraction in volume when one gram of ice melts is 0·09 cc. Latent heat of ice = 80 cal/g. Calculate the specific heat of the solid. [**Ans.** 0·5 cal/g°-C]

20. Calculate how much steam from water boiling at 100°C will just melt 200 g of wax at 15°C. (Melting point of wax = 55°C, Sq. heat of wax = 0·7, Latent heat of fusion of wax = 35 cal per g) [**Ans** 21·54 g]

5

Nature of Heat

5·1 Introduction

In the previous chapters the various effects of heat and its properties have been discussed. At this stage it becomes necessary to formulate a cogent theory to explain the different heat phenomena and to see how far the proposed theory can explain the vast amount of data collected experimentally and otherwise. The theory should satisfactorily explain, primarily the following observed facts (*a*) thermal expansion, (*b*) conservation of heat energy. When there is transfer of heat between two bodies the heat lost by one body is equal to the heat gained by the other, (*c*) specific heat of bodies, (*d*) thermal capacity of bodies, (*e*) change of state from solid to liquid or liquid to gas, (*f*) propagation of heat radiations in space with the velocity of light.

Two rival theories have been proposed to explain the properties and the effects of heat. The two theories are : (*i*) *Caloric theory of heat* and (*ii*) *Dynamic theory* or the *Kinetic theory of heat*. The caloric theory of heat assumes heat as some fluid and in the course of heat transfer from one body to another, this fluid is transferred. This theory held ground till the end of the eighteenth century.

The experiments of Joule, Rumford and Davy have shown that heat is a form of energy associated with the mechanical motion of material particles Thus the kinetic theory of matter favoured the dynamical theory in preference to the caloric theory.

5·2 Caloric Theory of Heat

According to this theory heat is considered to be invisible, weightless fluid called *caloric*. This fluid can be produced when substances are burnt and this fluid can flow from a hot body to a cold body The hot body is assumed to have more of this fluid and the cold body comparatively less. When a hot body is brought in contact with a cold body, the fluid flows from the hotter to the colder body, just as water flows from higher to lower level. This fluid is supposed to be all-pervading, uncreatable and indestructible. The fluid is highly elastic and the particles of this fluid repel one another very strongly. When this fluid is added to a body its temperature rises and when the fluid is removed its temperature decreases. This fluid occupies the interstices of matter. Just as water can be obtained from a sponge by squeezing, heat can also be obtained from a body by extracting the caloric by friction. The caloric theory could explain in a crude and elementary way, different heat phenomena like conduction, thermal conductivity, latent heat etc.

5·3 Failure of Caloric Theory

The caloric theory held ground till the end of the eighteenth century. The work of Rumford, an artillery engineer began to cast doubts about the validity of the caloric theory. Rumford was engaged in the supervision of boring of cannon for the government of Bavaria. The boring process produced tremendous amount of heat and to prevent this overheating the cannon was immersed in water. Even this water boiled off during the process and the boring process had to be stopped. According to the caloric theory, it was admitted that the caloric had to be supplied to water to raise its temperature to the boiling point. The continuous extraction of caloric during the process of boring was explained on the hypothesis that when matter was finely subdivided its capacity to hold the caloric decreases, and the caloric thus released causes the water to boil.

It was interesting to note that the water surrounding the cannon continued to boil even after the borer became blunt and when there was no further cutting This proves that even a blunt drill continuously produced an inexhaustible supply of heat which is contrary to the explanation given on the basis of the caloric theory. Further, while explaining the production of heat the conservation principle which is very vital to the concepts of physics has not been kept in mind. During the boring process, mechanical work was continuously expended and caloric was continuously extracted. Rumford's observation gave him an opportunity of eliminating the two cases of non-conservation. This process of elimination is possible only when heat also is considered as a form of energy. What is involved is not the disappearance of the mechanical energy and the appearance of heat energy but it is the transformation of one form of energy into another. Rumford made some measurements regarding the work done and the corresponding heat produced, though his experiments lacked precision It was later the work of Joule during the years 1843 to 1878 that established the equivalence of heat and work as two forms of energy

5·4 Mechanical Equivalent of Heat (Joule's Experiments)

James Prescott Joule (1818—1889) performed a series of experiments to prove convincingly that heat is also a form of energy. His findings that there is a definite equivalence between the work done and the corresponding amount of heat and any other form of energy, put an end to the controversy that existed between the caloric theory and the dynamical theory of heat. The dynamical theory of heat was firmly established.

He developed the argument that if an amount of work W (or any other form of energy) disappears a definite quantity of heat H is produced.

$$W \propto H$$

or

$$W = JH$$

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

The constant J is called the mechanical equivalent of heat. The mechanical equivalent of heat (J) is defined as the amount of work done to produce a unit quantity (1 calorie) of heat. The value of J in C.G.S. system is $4{\cdot}18 \times 10^7$ ergs/calorie. In the M.K.S. system its value is 4·18 joules/calorie.

Joule's method for determining the mechanical equivalent of heat. The apparatus consists of a calorimeter with the fixed blades a, a etc. fixed to the calorimeter radially. S is a spindle which is fitted with the vanes b, b radially and these vanes are called the movable vanes (Fig. 5·1).

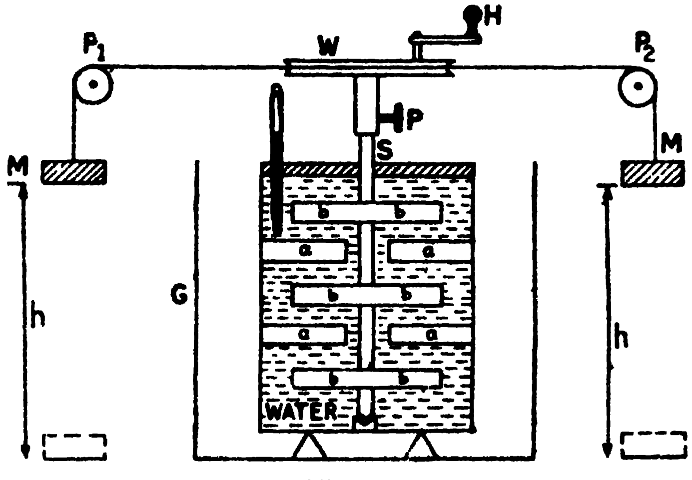


Fig. 5·1

When the spindle rotates, the vanes a, a are stationary and the vanes b, b rotate. The water between any two vanes gets warmed up due to the frictional forces between the two vanes.

W is a wheel with a handle H, which can rotate about a vertical axis. Two strings are wound in the same direction over the drum W and these strings pass over the pulleys P_1 and P_2 and they carry the masses M, M at the other ends.

When the masses are moved up and left free, they move down due to gravity, thus rotating the drum and the spindle. When the masses are moved up the pin P is removed and when the masses *move down the pin P is fixed. This is done because when the masses are moved up, the work done is not taken into calculation.*

Let the masses move down by a distance of h cm

Loss of potential energy of the two masses $= 2\ Mgh$

If the masses fall down n times, the loss of energy

$$= n \times 2Mgh$$

Let the velocity of the masses at the end of the fall be v cm/s

To find v, the time taken by the masses to fall through a height h is noted. The average velocity $= \frac{h}{t}$. Therefore the velocity at the end of the fall will be twice the average velocity because the initial velocity is zero.

$$\therefore \qquad v = 2\left(\frac{h}{t}\right)$$

Kinetic energy of the two masses

$$= 2 \times \tfrac{1}{2}Mv^2$$

$$= Mv^2$$

For n times the $KE = n \times Mv^2$

$\therefore$ Energy used up in heating the water and the calorimeter,

$$W = n[2Mgh - Mv^2]$$

Let the total water equivalent of the calorimeter, water, fixed vanes, movable vanes etc. be w

Initial temperature $= \theta_1$

Final temperature $= \theta_2$

Heat produced $= H$

$$= w(\theta_2 - \theta_1)$$

$\therefore$ J, the mechanical equivalent of heat

$$= \frac{W}{H}$$

$$= \frac{n[2Mgh - Mv^2]}{w(\theta_2 - \theta_1)}$$

The value of J as a mean of a number of observations is taken. The value of J is $4{\cdot}18 \times 10^7$ ergs/cal.

5·5 Rowland's Experiment

Rowland found the value of J accurately in the year 1879. In the Joule's original experiment there were two main defects. (*i*) The rate of rise of temperature was small [about 0·6°C per hour] and so the loss of heat due to radiation was appreciable and (*ii*) the observed temperatures were not corrected to the standard gas scale.

Rowland's apparatus consists of a calorimeter C fitted with vanes on its inner side (Fig. 5·2). The calorimeter is suspended from a torsion wire. D is a drum over which cords are wound. The ends of the cords are connected to the masses M and M, passing over the pulleys. The cords leave the drum at diametrically opposite points. Thus a couple is applied on the calorimeter. AB is a rod having sliding masses m and m and are used to increase the moment of inertia of the system.

The spindle S has paddles attached to it and it is rotated with a very high speed with the help of a steam engine. The counters C_1 and C_2 are used to measure the number of rotations of the spindle. A sensitive thermometer T already corrected with a standard gas

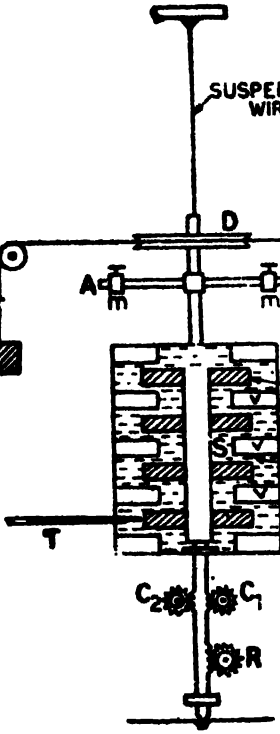


Fig. 5·2

scale is used to measure the temperature of water in the calorimeter. The calorimeter is surrounded by a water jacket in which water is circulated at constant temperature to find the cooling correction.

The initial temperature of water in the calorimeter is noted. The spindle is set rotating and the masses M, M are adjusted quickly so that the calorimeter does not rotate and remains in the equilibrium position. The rotation is continued till there is sufficient rise in temperature. Suppose the initial temperature of water is θ_1 and after n rotations of the spindle, its temperature is θ_2. The rotations are measured with the help of the counters. The couple applied by the masses $= MgD$. Here D is the diameter of the drum.

For n rotations, the work done,

$$W = 2\pi n\, Mg\, D$$

Heat produced, $\quad H = (m+w)(\theta_2-\theta_1)$

Here m is the mass of water and w is the water equivalent of the calorimeter, the vanes, the paddles and the spindle

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

$$= \frac{2\pi n\, MgD}{(m+w)(\theta_2-\theta_1)} \text{ ergs/cal}$$

Following corrections are to be applied (*i*) cooling correction and (*ii*) correction for the torsional couple, *i e*, the weight Mg in air, should be reduced to vacuum

The results obtained by Rowland at various temperatures were as follows

Temperature °C	*J (joules per calorie)*
10	4.196
15	4.188
20	4.181
25	4.176
30	4.174
35	4.175

The mean value of J is taken as 4.18 joules per calorie or 4.18×10^7 ergs per calorie

5.6 Searle's Friction Cone Method

The apparatus consists of two truncated friction cones A and B made of brass. The cone B is fixed to an ebonite disc C fitted inside a brass cylinder E. F is an ebonite ring which holds B in position. S is a spindle attached to the base of the cylinder E. The spindle is rotated at high speed by hand or with an electric motor. The number of rotations made by the spindle is measured with the help of the counters C_1 and C_2 (Fig. 5.3)

A grooved wooden disc D is fixed to the inner cone A with the help of pins passing through the iron ring I. The iron ring also provides the necessary weight for the cone A to be in its position. A cord passes around the groove of the disc D and the other end is connected to a mass M. The chord passes over a pulley. A mercury thermometer calibrated to gas scale is used to measure the temperature of water in the cone A

The outer cone B is rotated with the help of the spindle and it tends to rotate the cone A. The mass M is adjusted quickly so that the cone A does not rotate. A couple Mgr is provided by the mass in the opposite direction. Due to friction, heat is produced and water in the cone *A* gets heated.

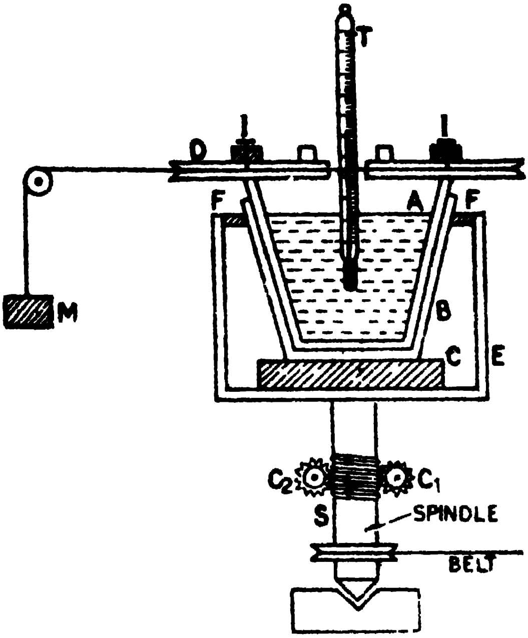


Fig. 5·3

Suppose,

Initial temperature of water $= \theta_1$

Final temperature of water $= \theta_2$

Rise in temperature $= (\theta_2 - \theta_1)$

Number of rotations made by the spindle $= n$

Mass of water $= m$

Water equivalent $= w$

Radius of the disc *D* $= r$

Work done, $W = 2\pi\, n\, (Mgr)$

Heat produced $H = (m+w)\,(\theta_2 - \theta_1)$

$$\therefore \qquad J = \frac{W}{H}$$

$$= \frac{2\pi n\, Mgr}{(m+w)\,(\theta_2 - \theta_1)} \qquad \ldots(i)$$

Radiation Correction. The time for which the spindle is rotated is noted. The fall in temperature is noted for the same time after the experiment. Let $\delta\theta$ be the fall in temperature. Then radiation correction $= (\delta\theta/2)$

$\therefore$ The correct rise in temperature

$$= \left[(\theta_2 - \theta_1) + \frac{\delta\theta}{2}\right]$$

$$\therefore \qquad J = \frac{2\pi n\, M g r}{(m+w)\left[(\theta_2-\theta_1)+\dfrac{\delta\theta}{2}\right]} \text{ ergs/cal}$$

5·7 Joule's Calorimeter (Determination of J)

The apparatus consists of a copper calorimeter containing water to about $\frac{2}{3}$ of its volume. A resistance coil R is immersed in water and the two ends of R are connected to two binding terminals fixed to the lid. A stirrer and a thermometer are inserted through holes in the lid.

The calorimeter is closed in a wooden box to minimize the loss of heat (Fig. 5·4).

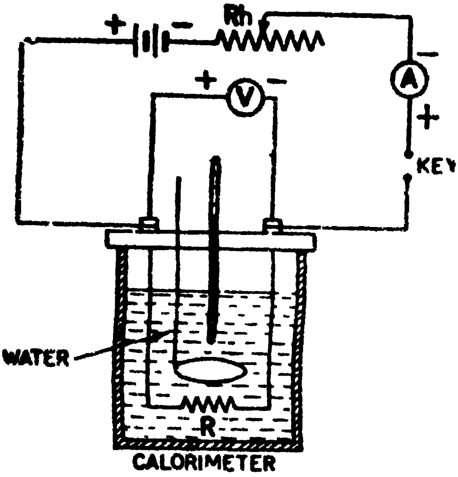


Fig. 5·4

The electrical connections are shown in Fig. 5 4. If a current of I amperes is passed through the resistance coil R at a potential difference of V volts for a time t seconds, then the amount of energy liberated $= VIt \times 10^7$ ergs.

Knowing the total water equivalent w, and the initial and final temperatures of the calorimeter θ_1 and θ_2, the heat produced H can be calculated

$$H = w(\theta_2-\theta_1)$$

To apply the radiation correction, the calorimeter is allowed to cool for the same interval of time t as that of the passage of current, and the fall in temperature θ_3 is noted. Half of this fall in temperature is added to the final observed temperature θ_2.

$\therefore$ Corrected final temperature $= \theta_2 + \dfrac{\theta_3}{2}$

Mechanical equivalent of heat

$$J = \frac{\text{Work done}}{\text{Heat produced}}$$

$$J = \frac{VIt \times 10^7}{w\left(\theta_2 + \frac{\theta_3}{2} - \theta_1\right)} \text{ ergs/cal}$$

In case, the resistance of the voltmeter is not high, the actual value of current passing through R is calculated, knowing the values of R and the reading of the voltmeter The drawback of this experiment is the small rate of rise of temperature due to low current that can be drawn from accumulators used as the source of supply

5·8 Callendar and Barnes Continuous Flow Method (Determination of J)

The Callendar and Barnes apparatus consists of a resistance coil R enclosed inside a narrow glass tube (Fig. 5·5). The two ends of the wire are connected to two thick copper connectors. Continuous flow of water can be maintained through the tube and the temperatures of inlet and outlet water are measured with thermometers T_1 and T_2 The central tube containing R is surrounded by a vacuum jacket which minimises the loss of heat by conduction and convection. The vacuum jacket is surrounded by an outer jacket through which water is circulated continuously. This ensures the loss of heat by radiation to be steady.

The coil R is connected in series with a battery, a rheostat, an ammeter and a key. A voltmeter is connected across the terminals of R For more accurate work, the current through the coil and the potential difference across its ends are measured using a potentiometer, initially calibrated with a standard cell.

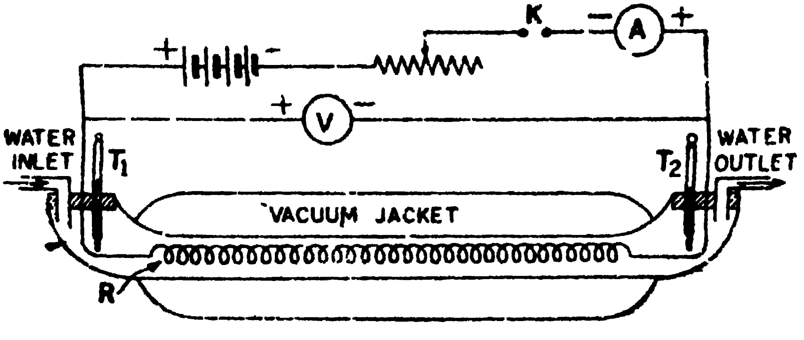


Fig. 5·5. Callendar and Barnes' Continuous Flow Apparatus.

When the rate of flow of water and the current passing through R are maintained constant, a steady state will be reached and the thermometers T_1 and T_2 will show constant readings. At this stage, the temperatures of every part of the apparatus will remain steady. When the thermometers T_1 and T_2 show constant readings, say θ_1 and θ_2, the mass of water (m) flowing in a time t seconds is measured. If S is the mean value of the specific heat of water between the temperatures θ_1 and θ_2 and H the quantity of heat lost by radiation etc , then the amount of heat produced by passage of electric current through the coil

$$= mS(\theta_2-\theta_1)+H \qquad ...(i)$$

If V and I are the voltmeter and ammeter readings then the amount of energy liberated in time t seconds $= VIt\times 10^7$ ergs. The corresponding quantity of heat produced

$$= \frac{VIt\times 10^7}{J} \text{ cals} \qquad ...(ii)$$

From (i) and (ii)

$$\frac{VIt\times 10^7}{J} = mS(\theta_2-\theta_1)+H \qquad ...(iii)$$

To eliminate H, a second set of observations is taken by altering the values of the current and the rate of flow of water such that the difference of temperature $\theta_2-\theta_1$ remains the same after the steady state is reached. If V', I' and m' are the corresponding values for the same time t, then

$$\frac{V'I't\times 10^7}{J} = m'S(\theta_2-\theta_1)+H \qquad ...(iv)$$

As the temperature difference $(\theta_2-\theta_1)$ is maintained the same in the two cases, the temperatures of the various parts of the apparatus will be the same and hence the loss of heat by radiation etc. will also be the same.

Subtracting (iv) from (iii)

$$\frac{(VI-V'I')t\times 10^7}{J} = (m-m')S(\theta_2-\theta_1)$$

$$J = \frac{(VI-V'I')t\times 10^7}{(m-m')S(\theta_2-\theta_1)} \text{ ergs/cal}$$

All the quantities in the above expression can be measured very accurately. With calibrated platinum resistance thermometers, the temperature difference can be measured with great precision. Similarly, the values of the current and the potential difference can also be measured very accurately. Thus, this method ensures an accurate determination of the value of J.

5·9 Jaegar and Steinwehr's Method

In 1921 Jaegar and Steinwehr performed an experiment to find the value of J accurately. Their method has an accuracy of 1 in 1,000 The value of J obtained by them is equal to $4\cdot186\times 10^7$ ergs per calorie.

The apparatus consists of a large cylinder containing about 50 kg of water. R is a heater coil and T is a sensitive platinum resistance thermometer calibrated to the gas scale. S_1 and S_2 are two electrically rotating stirrers (Fig. 5 6). The cylinder is surrounded by an outer jacket through which water is circulated at constant temperature. This will help in estimating the cooling correction accurately. The current is measured with a standard resistance placed in series with the heating resistance R. The potential difference across the standard resistance is obtained with a sensitive potentiometer initially calibrated with a standard cell. The time for which the current is passed is measured accurately with a chronograph.

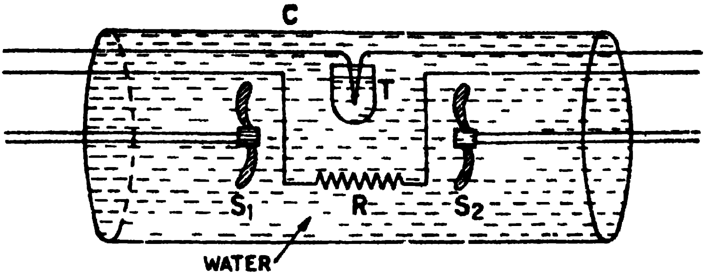


Fig. 5 6

Let the potential difference across R be V volts and the current flowing for t seconds be I amperes.

Work done $= VIt$ joules

Heat produced $= (m+w)(\theta_2-\theta_1)$

Here m is the mass of water and w is the water equivalent of the apparatus

$$J = \frac{VIt}{(m+w)(\theta_2-\theta_1)} \text{ joules/calorie}$$

or

$$J = \frac{VIt\times 10^7}{(m+w)(\theta_2-\theta_1)} \text{ ergs/calorie}$$

This method has the following advantages :—

(1) The mass of water used is very large. Hence the correction for the thermal capacity of the vessel is small.

(2) A small rise in temperature of the order of 1 4°C is obtained. This will enable to apply the cooling correction accurately because Newton's law of cooling is applicable.

(3) Efficient stirring of water is provided. Thus the temperature of water and the calorimeter remains uniform.

(4) As the surrounding temperature of the cylinder is kept constant by circulating water at constant temperature, cooling correction can be accurately determined.

Example 3 *A lead bullet strikes a target with a velocity of* 480 m/s. *If the bullet falls dead, calculate the rise in temperature, assuming that all the heat developed is equally shared between it and the target (Sp heat of lead = 0 0[illegible])*

Suppose mass of the bullet $= m$ grams

Rise in temperature $= \theta$

Velocity $v = 480$ m/s

$= 48{,}000$ cm/s

Work done $= \frac{1}{2} mv^2$

$= \frac{1}{2} m\,(48{,}000)^2$ ergs

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

$$= \frac{m(48{,}000)^2}{2 \times 4{\cdot}2 \times 10^7} \text{ cals.}$$

Half of this heat energy is used to raise the temperature of the bullet.

$$\therefore \quad \text{Useful heat } H = \frac{m(48{,}000)^2}{2 \times 2 \times 4{\cdot}2 \times 10^7} \text{ cals}$$

$$mS\theta = \frac{m(48{,}000)^2}{4 \times 4{\cdot}2 \times 10^7}$$

$$\theta = \frac{48{,}000 \times 48{,}000}{0{\cdot}03 \times 4 \times 4{\cdot}2 \times 10^7}$$

$$= \mathbf{457{\cdot}14°C}$$

Example 5·2 *Calculate the increase in energy per atom of aluminium in ergs when the temperature of a piece of aluminium increases by 1°C (27 g of aluminium contains 6×10^{23} atoms and sp heat of aluminium = 0·22).*

Heat required to raise the temperature of 27 grams of aluminium by 1°C

$= 27 \times 0{\cdot}22 \times 1$ cal

Energy gained by 6×10^{23} atoms of aluminium

$= 27 \times 0{\cdot}22 \times 4{\cdot}2 \times 10^7$ ergs

Increase in energy per atom of aluminium

$$= \frac{27 \times 0{\cdot}22 \times 4{\cdot}2 \times 10^7}{6 \times 10^{23}} \text{ ergs}$$

$$= \mathbf{4158 \times 10^{-19} \text{ ergs}}$$

Example 5·3 *What will be the rise in temperature of water if it falls from a height of 50 metres, assuming that all the energy is used in heating the water?* (*Punjab 1966*)

$h = 50$ metres $= 5{,}000$ cm

Suppose, rise in temperature $= \theta$°C

Mass of water $= m$

Work done $= W = mgh$

$= m \times 980 \times 5{,}000$ ergs

$$\text{Heat produced} = H = mS\theta$$
$$= m \times 1 \times \theta \text{ calories}$$
$$W = JH$$
$$m \times 980 \times 5{,}000 = 4{\cdot}2 \times 10^7 \times m \times \theta$$
$$\theta = \frac{980 \times 5{,}000}{4{\cdot}2 \times 10^7}$$
$$= 0{\cdot}117°\text{C}$$

5·10 Kinetic Theory of Matter

The experiments on the conversion of work into heat have shown clearly that heat is a form of energy. This energy is connected with the motion of molecules of which the matter is made of. Kinetic theory of matter gives an explanation to the nature of this motion and the nature of heat energy.

According to Kinetic theory of matter, every substance (in the form of solid, liquid or gas) consists of a very large number of very small particles called the molecules. The molecules are the smallest particles of a substance that can exist in free state. The molecules possess the characteristic properties of the parent substance. The molecules are in a state of continuous motion with all possible velocities. The velocity of the molecules increases with rise in temperature.

The energy possessed by the molecules can be of two forms, kinetic or potential. When the stop-cock of an evacuated flask is opened air rushes in quickly to fill in the space. This shows that the molecules possess rapid motion and hence they possess kinetic energy. When a solid expands on heating, the molecules are pulled apart against the forces of intermolecular expansion. The amount of work done in separating the molecules to larger distances manifests itself as the potential energy of the molecules. Thus the amount of heat given to a solid substance increases the energy of the molecules and this increase in energy is partly kinetic and partly potential.

Thus, the kinetic theory of matter is based on the following three points : (*i*) matter is made up of molecules, (*ii*) molecules are in rapid motion, and (*iii*) molecules experience forces of attraction between one another.

The validity and the soundness of any theory depends on its capability to explain the observed facts, *viz.*, the three states of matter, expansion, change of state and conduction.

5·11 The Three States of Matter

Solid. In the case of a solid the intermolecular distances are small and hence the forces of intermolecular attraction are large. The only motion permissible to a molecule is oscillation or vibration about its mean position which is fixed. Hence a solid has definiee size and shape. Heating a solid means giving more energy to the molecules. This will enable the molecules to vibrate more violently about their mean position. The molecules move further apart and this results in the expansion of the solid. With the supply of more heat to the solid, the amplitude of vibration of the molecules increases to such an extent that the molecules will be free to leave their mean position because the kinetic energy of the molecules is greater than the potential energy due to the forces of intermolecular attraction. Now the molecules are free to move about within the body of the substance and this corresponds to the liquid state of the substance. The amount of heat supplied, which is equivalent to the work done in pulling the molecules apart against the forces of intermolecular attraction, determines the latent heat of fusion of the solid.

Liquid. In a liquid, the molecules are farther apart than the solid. The molecules are not confined to any fixed mean position. They are free to move about within the volume of the liquid. Hence the liquids have their own size but no shape.

The definite size of the liquid is due to the mutual forces of attraction between the molecules. The molecules present on the surface of the liquid experience a resultant downward force due to the presence of the molecules present within the sphere of influence and hence the surface of a liquid behaves as a stretched membrane. This is the phenomenon of surface tension. The volume of the liquid is fixed at a given temperature but the molecular distances are comparatively larger than that of a solid. Therefore the molecules experience less force of attraction and they can occupy any position within the liquid. Hence the liquid occupies the shape of the containing vessel.

The molecules are always in a state of random motion. They collide with each other and they may or may not change their respective kinetic energies. As already explained, every molecule on the surface of the liquid is held in its position as a result of the forces of intermolecular attraction and surface tension. Due to the collisions a certain molecule may acquire more energy than the energy with which it is held. As soon as this happens, the molecule flies off, *i.e.*, it leaves the liquid surface. This is called evaporation If no external heat is supplied it is obvious that the mean kinetic energy of the molecules decreases and the temperature of the liquid falls. This explains cooling caused by evaporation. If the moving vapour molecules come near to each other at sufficiently low velocities, they experience a greater magnitude of force of attraction. The molecules coalesce and this results in condensation. Rate of evaporation increases with increase in temperature of the liquid and decrease in pressure over the liquid surface.

Gas. In the case of a gas, the inter-molecular distances are much larger than that of a solid or a liquid and the molecules of a gas are free to move about in the entire space available to them. Hence a gas has no shape or size. If the space occupied by a gas is increased, the gas will occupy the whole of the new space uniformly. This is due to the fact that the molecules possess rapid random motion and the force of inter-molecular attraction is negligibly small The molecules move about independently in straight lines and the only restriction to this movement is collision with another molecule or collision with the walls of the containing vessel. In a gas the more predominant factor is the movement of the molecules than the force of attraction between the molecules.

5·12 Concept of Ideal or Perfect Gas

At very low pressures, the forces of inter-molecular attraction are negligible. Therefore, at low pressures only, a real gas obeys the equation $PV = RT$. An ideal gas can be defined as a real gas at low pressure. For a real gas the internal energy is a function of pressure and temperature. By definition, the ideal gas should satisfy the equation

$$PV = RT \qquad \ldots(i)$$

and

$$\left[\frac{dU}{dP}\right]_T = 0 \qquad \ldots(ii)$$

$$\left(\frac{dU}{dV}\right)_T = \left[\frac{dU}{dP}\right]_T \left[\frac{dP}{dV}\right]_T$$

From equation (*i*)

$$\frac{dP}{dV} = -\frac{RT}{V^2}$$

$$= -\left[\frac{RT}{V}\right]\left[\frac{1}{V}\right] = -\frac{P}{V}$$

$$\therefore \quad \left(\frac{dU}{dV}\right)_T = \left[\frac{dU}{dP}\right]_T \left[-\frac{P}{V}\right]_T \qquad \ldots(iii)$$

As $\left(-\frac{P}{V}\right)$ is not equal to zero and

$$\left[\frac{dU}{dP}\right]_T = 0$$

$$\therefore \quad \left[\frac{dU}{dV}\right]_T = 0 \qquad \ldots(iv)$$

Since for an ideal gas $\left[\frac{dU}{dP}\right]_T$ and $\left[\frac{dU}{dV}\right]_T$ are both equal to zero, the internal energy of an ideal gas is a function of temperature only.

$$\therefore \quad U = f(T) \qquad \ldots(v)$$

In a large number of calculations, a real gas can be taken approximately as an ideal gas. This involves an error that can be tolerated in the calculations. For all practical purposes, real gases below a pressure of two atmospheres can be considered as ideal gases. A saturated vapour in equilibrium with its own liquid can be considered to have the properties of an ideal gas. The error involved is low.

5·13 Kinetic Theory of Gases

The continuous collision of the molecules of the gas with the walls of the containing vessel and their reflection from the walls results in the change of momentum of the molecules. According to Newton's second law of motion, the rate of change of momentum per unit area of the wall surface corresponds to the force exerted by the gas per unit area. The force per unit area measures the pressure of the gas.

Postulates of the kinetic theory of gases

(*i*) The gas is composed of small indivisible particles called molecules The properties of the individual molecules are the same as that of the gas as a whole.

(*ii*) The distance between the molecules is large as compared to that of a solid or liquid and hence the forces of inter-molecular attraction are negligible

(*iii*) The molecules are continuously in motion with varying velocities and the molecules move in straight lines between any two consecutive collisions The collisions do not alter the molecular density of the gas, i e , on the average the number of molecules present in a unit volume remains the same. Also, the molecules do not accumulate at any place within the volume of the gas

(*iv*) The size of the molecules is infinitesimally small as compared to the average distance traversed by a molecule between any two consecutive collisions The distance between any two consecutive collisions is called free path and the average distance is called the mean free path The mean free path is dependent on the pressure of the gas. If the pressure is high the mean free path is less and if the pressure is low the mean free path is more.

(*v*) The time of impact is negligible in comparison to the time taken to traverse the free path.

(*vi*) The molecules are perfectly nard elastic spheres and the whole of their energy is kinetic.

5·14 Expression for the Pressure of a Gas

As mentioned earlier, the continuous impact of the molecules on the walls of the containing vessel accounts for the pressure of the gas.

Consider a cubical vessel *ABCDEFGH* of side l cm containing the gas (Fig. 5·7). The volume of the vessel and hence that of the gas is l^3 cc. Let n and m represent the very large number of molecules present in the vessel and the mass of each molecule respectively.

Consider a molecule P moving in a random direction with a velocity C_1. The velocity can be resolved into three perpendicular components u_1, v_1 and w_1 along the X, Y and Z axes respectively. Therefore,

$$C_1^2 = u_1^2 + v_1^2 + w_1^2$$

The component of the velocity with which the molecule P will strike the opposite face $BCFG$ is u_1 and the momentum of the molecule is mu_1. This molecule is reflected back with the same momentum mu_1 in an opposite direction and after traversing a distance l will strike the opposite face $ADEH$.

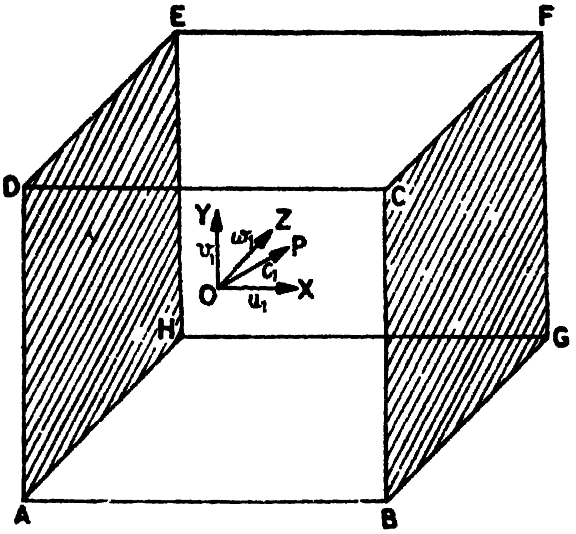


Fig. 5·7

The change in momentum produced due to the impact is

$$mu_1-(-mu_1) = 2mu_1$$

As the velocity of the molecule is u_1, the time interval between two successive impacts on the wall $BCFG$ is

$$\frac{2l}{u_1} \text{ seconds}$$

∴ No. of impacts per second

$$= \frac{1}{\frac{2l}{u_1}}$$

$$= \frac{u_1}{2l}$$

Change in momentum produced in one second due to the impact of this molecule is

$$2mu_1 \times \frac{u_1}{2l} = \frac{mu_1^2}{l}$$

The force F_X due to the impact of all the n molecules in one second

$$= \frac{m}{l}\left[u_1^2+u_2^2+\ldots+u_n^2\right]$$

Force per unit area on the wall *BCFG* or *ADEH* is equal to the pressure P_X

$$P_X = \frac{m}{l \times l^2}(u_1^2+u_2^2+u_3^2+\ldots\ldots+u_n^2)$$

Similarly the pressure P_Y on the walls *CDEF* and *ABGH* is given by

$$P_Y = \frac{m}{l^3}(v_1^2+v_2^2+\ldots\ldots+v_n^2)$$

and the pressure P_Z on the walls *ABCD* and *EFGH* is given by

$$P_Z = \frac{m}{l^3}(w_1^2+w_2^2+\ldots\ldots+w_n^2)$$

As the pressure of a gas is the same in all directions, the mean pressure P is given by

$$\begin{aligned} P &= \frac{P_X+P_Y+P_Z}{3} \\ &= \frac{m}{3l^3}\Big[(u_1^2+v_1^2+w_1^2)+(u_2^2+v_2^2+w_2^2) \\ &\qquad +(u_3^2+v_3^2+w_3^2)+\ldots\ldots \\ &\qquad +(u_n^2+v_n^2+w_n^2)\Big] \\ &= \frac{m}{3l^3}\Big[C_1^2+C_2^2+C_3^2+\ldots\ldots C_n^2\Big] \qquad \ldots(i) \end{aligned}$$

But volume, $V = l^3$. Let C be the root-mean-square velocity of the molecules (R.M.S. velocity).

Then $$C^2 = \frac{C_1^2+C_2^2+C_3^2+\ldots\ldots C_n^2}{n}$$

or $$nC^2 = C_1^2+C_2^2+C_3^2+\ldots\ldots C_n^2$$

Substituting this value in equation (*i*), we get

$$P = \frac{m.nC^2}{3V} \qquad \ldots(ii)$$

But $M = mn$ where M is the mass of the gas of volume V, m is the mass of each molecule and n is the number of molecules in a volume V.

$$P = \frac{MC^2}{3V}$$

or $$P = \frac{1}{3}\rho C^2 \qquad \ldots(iii)$$

$\because$ $\frac{M}{V} = \rho$ the density of the gas.

From equation (*iii*)

$$C^2 = \frac{3P}{}$$

or $$C = \sqrt{\frac{3P}{\rho}} \qquad \ldots(iv)$$

[Note. R.M.S. velocity *C* is the square root of the mean of the squares of the individual velocities and it is not equal to the mean velocity of the molecules.]

TABLE
Molecular Velocities at 0°C

Gas	*Molecular Weight*	*Root mean square velocity in* cm/s
Hydrogen	**2·016**	$18{\cdot}4 \times 10^4$
Helium	**4**	$13{\cdot}1 \times 10^4$
Nitrogen	**28**	$4{\cdot}95 \times 10^4$
Oxygen	**32**	$4{\cdot}61 \times 10^4$
Argon	**40**	$4{\cdot}14 \times 10^4$
Carbon dioxide	**44**	$3{\cdot}95 \times 10^4$
Chlorine	**71**	$3{\cdot}11 \times 10^4$

R.M.S. velocity of hydrogen

The density of hydrogen at N.T.P. is 0·000089 g/cc. Therefore *C* for hydrogen can be calculated as follows :

$$C = \sqrt{\frac{3P}{\rho}}$$

$$= \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981}{0{\cdot}000089}}$$

$$= 1{\cdot}84 \times 10^5 \text{ cm/s}$$

(*b*) For oxygen the density at N.T.P.

$$= 16 \times 0{\cdot}000089$$

$$\therefore \quad C \text{ for oxygen} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981}{16 \times 0{\cdot}000089}}$$

$$= 4{\cdot}6 \times 10^4 \text{ cm/s}$$

(*c*) For air the density at N.T.P. is 0·001293 g/cc

$$\therefore \quad C \text{ for air} = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 981}{0{\cdot}001293}}$$

$$= \mathbf{4{\cdot}850 \times 10^4 \text{ cm/s}}$$

Example 5·4 *Calculate the number of molecules in one* c.c. *of oxygen at N.T.P. using the following data :—*

Density of mercury $= 13{\cdot}6$ g/cm^3
R.M.S. *velocity of oxygen molecules at* $0°$C
$= 4{\cdot}62 \times 10^4$ cm/s
Mass of one molecule of oxygen $= 52{\cdot}8 \times 10^{-24}$ g

$$P = \frac{1}{3}\rho C^2$$

Let the mass of each molecule be m and the number of molecules in one cc $= n$

$$\therefore \qquad P = \frac{1}{3} mnC^2$$

$$n = \frac{3P}{m\bar{C}^2}$$

Here

$$P = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$m = 52{\cdot}8 \times 10^{-24} \text{ g}$$
$$C = 4{\cdot}62 \times 10^4 \text{ cm/s}$$
$$\therefore \qquad n = \frac{3 \times 76 \times 13{\cdot}6 \times 980}{52{\cdot}8 \times 10^{-24} \times (4{\cdot}62 \times 10^4)^2}$$
$$\mathbf{n = 2{\cdot}697 \times 10^{19}}$$

5 15 Kinetic Energy per Unit Volume of a Gas

$$P = \frac{1}{3}\rho C^2$$
$$= \frac{2}{3} \cdot \frac{1}{2}\rho C^2$$
$$= \frac{2}{3} \cdot E$$

where $E = \frac{1}{2}\rho C^2$ and is equal to the kinetic energy per unit volume of the gas. ρ is the mass per unit volume. Hence, the pressure of a gas is numerically equal to two-thirds of the mean kinetic energy of translation of a unit volume of the molecules

5 16 Kinetic Interpretation of Temperature

The pressure of a gas, according to the kinetic theory, is

$$P = \frac{1}{3}\rho C^2$$
$$P = \frac{1}{3}\frac{MC^2}{V}$$
$$PV = \frac{1}{3} MC^2$$

Consider 1 gram molecule of the gas at a temperature T K

$$PV = RT$$
$$\therefore \qquad \frac{1}{3} MC^2 = RT$$
$$\frac{1}{2}MC^2 = \frac{3}{2}RT \qquad \ldots(i)$$

Let the mass of each molecule be m and Avogadro's number be N.

$$M = m \times N$$

$$\frac{1}{2} mNC^2 = \frac{3}{2} RT$$

$$\frac{1}{2} mC^2 = \frac{3}{2} \frac{R}{N} T$$

$$= \frac{3}{2} kT \qquad \ldots(ii)$$

Here k is called Boltzmann's constant.

Thus, from equation (*ii*), the mean kinetic energy of a molecule is directly proportional to the absolute temperature of a gas. When the temperature of the gas is increased, the mean kinetic energy of the molecules increases. When heat is withdrawn from a gas, the mean kinetic energy of the molecules decreases. Thus, at absolute zero temperature, the kinetic energy should be zero. It means at absolute zero temperature, the molecules are in a perfect state of rest and have no kinetic energy. But before the absolute zero temperature is reached, all gases change their state to liquids and solids.

Also from equation (*ii*), $C^2 \propto T$

It means that the root mean square velocity of the molecules is also directly proportional to the square root of the absolute temperature.

Example 5·5 *At what celsius temperature will oxygen molecules have the same root mean square velocity as that of hydrogen molecules at —100°C ?*

The energy of a gas molecule is,

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

For hydrogen molecules

$$\frac{1}{2} m_1C_1^2 = \frac{3}{2} kT_1 \qquad \ldots(i)$$

For oxygen molecules

$$\frac{1}{2} m_2C_2^2 = \frac{3}{2} kT_2 \qquad \ldots(ii)$$

Dividing (*i*) by (*ii*)

$$\frac{m_1C_1^2}{m_2C_2^2} = \frac{T_1}{T_2} \qquad \ldots(iii)$$

Here $C_1 = C_2$

$$T_1 = -100°\text{C}$$

$$= -100+273$$

$$= 173 \text{ K}$$

$$T_2 = ?$$

$$\frac{m_2}{m_1} = 16$$

From equation (*iii*)

$$T_2 = \frac{m_2 C_2^2 T_1}{m_1 C_1^2}$$

$$T_2 = 16 \times 173$$

$$= 2768 \text{ K}$$

$$T_2 = 2768 - 273$$

$$= \mathbf{2495°C}$$

Example 5·6 *Calculate the* RMS *velocity of the oxygen molecules at 27°C.*

First calculate the *RMS* velocity of oxygen at N.T.P.

$$C = \sqrt{\frac{3P}{\rho}}$$

Here

$$P = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$\rho = 16 \times 0{\cdot}000089$$

$$\therefore \quad C = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 980}{16 \times 0{\cdot}000089}}$$

$$C = 4{\cdot}6 \times 10^4 \text{ cm/s}$$

Let the *RMS* velocity of the molecules at 27°C be C_1

$$\therefore \quad \frac{C_1}{C} = \sqrt{\frac{T_1}{T}}$$

$$C_1 = C \times \sqrt{\frac{T_1}{T}}$$

Here

$$C = 4{\cdot}6 \times 10^4 \text{ cm/s}$$

$$T = 273 \text{ K}$$

$$T_1 = 27°\text{C}$$

$$= 27 + 273$$

$$= 300 \text{ K}$$

$$C_1 = 4{\cdot}6 \times 10^4 \sqrt{\frac{300}{273}}$$

$$C_1 = \mathbf{4{\cdot}84 \times 10^4 \text{ cm/s}}$$

5·17 Derivation of Gas Equation

From kinetic theory,

$$P = \frac{1}{3} \rho C^2$$

$$P = \frac{1}{3}\frac{M}{V}C^2$$

$$PV = \frac{1}{3}MC^2$$

Consider one gram molecule of a gas at an absolute temperature T. The mean energy of the molecules

$$= \frac{1}{2}MC^2$$

$$= \frac{1}{2}NmC^2$$

$$\therefore \quad PV = \frac{1}{3}NmC^2$$

$$= \frac{2}{3}N.\frac{1}{2}.mC^2$$

Mean kinetic energy of a molecule

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

$$= \frac{3}{2}kT$$

$$\therefore \quad PV = \frac{2}{3}N.\frac{3}{2}kT$$

$$PV = NkT$$

But $\quad N \times k = R$

$$\therefore \quad PV = RT \qquad \ldots(ii)$$

Note on the Gas Equation.

In the gas equation

$PV = RT$

P is in dynes/sq cm

$R = 8{\cdot}31 \times 10^7$ ergs/g mol-K

T is in K

V is the volume in cc per gram molecule.

Example 5·7 *Calculate the volume occupied by 3·2 grams of oxygen at 76* cm *of* Hg *and 27°C*

Here $\quad P = 76 \times 13{\cdot}6 \times 980$ dynes/sq cm

$T = 27 + 273$

$= 300$ K

$R = 8{\cdot}31 \times 10^7$ ergs/g mol-K

$PV = RT$

$$V = \frac{8{\cdot}31 \times 10^7 \times 300}{76 \times 13{\cdot}6 \times 980} \text{ cc per g-mol}$$

$V = 24610$ cc per g mol

Volume for 3·2 g of oxygen $= v$

$$= \frac{24610 \times 3{\cdot}2}{32}$$

$$= \mathbf{2461\ cc}$$

5·18. Derivation of Gas Laws

(*i*) ***Boyle's Law***

According to the kinetic theory,

$$P = \frac{1}{3}\rho C^2$$

$$P = \frac{1}{3}\frac{M}{V}C^2$$

$$PV = \frac{1}{3}MC^2 \qquad \ldots(i)$$

At a constant temperature T, C^2 is constant. Therefore at a constant temperature

$$\frac{1}{3}MC^2 = \text{constant}$$

Hence $\qquad PV = \text{const.} -$ at constant temperature.

(*ii*) ***Charles' Law***

According to the kinetic theory

$$P = \frac{1}{3}\rho C^2$$

$$P = \frac{1}{3}\frac{M}{V}C^2$$

$$PV = \frac{1}{3}M\,C^2$$

Consider one gram molecule of a gas at absolute temperature T.

$$M = mN$$

$$PV = \frac{1}{3}NmC^2 \qquad \ldots(i)$$

The mean kinetic energy of a molecule

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

$$mC^2 = 3kT$$

Substituting this value in equation (*i*),

$$\therefore \qquad PV = NkT \qquad \ldots(ii)$$

where N is the Avogadro's number and k is the Boltzmann's constant.

If $\qquad P$ is constant,

$$V \propto T$$

It means that for a given mass of gas, the volume is directly proportional to the absolute temperature provided the pressure remains constant. This is Charles' Law.

(iii) Regnault's Law

From equation (*ii*)

$$PV = NkT$$

When V is constant,

$$P \propto T$$

It means that for a given mass of gas, the pressure is directly proportional to its absolute temperature provided the volume remains constant.

Example 5·8 *Show that n, the number of molecules per unit volume of an ideal gas is given by*

$$n = \frac{PN}{RT}$$

where N is Avogadro's number.

For an ideal gas, for one gram molecule of a gas,

$$PV = RT$$

But $R = Nk$

$$PV = NkT.$$

Let n be the number of molecules per cc. In that case,

$$P = nkT$$

$$\therefore \quad n = \frac{P}{kT}$$

But $k = \frac{R}{N}$

$$\therefore \quad n = \frac{PN}{RT}$$

Example 5·9. *Calculate the number of molecules in one cubic metre of an ideal gas at* N.T.P.

Let the number of molecules per cc be n.

$$n = \frac{PN}{RT}$$

Number of molecules in one cubic metre volume

$$x = n \times 10^6$$

$$x = \frac{PN \times 10^6}{RT}$$

Here $P = 76 \times 13{\cdot}6 \times 980$ dynes/cm^2

$$N = 6{\cdot}023 \times 10^{23}$$

$$R = 8{\cdot}31 \times 10^7 \text{ erg/g mol-K}$$

$$T = 273 \text{ K}$$

$$x = \frac{76 \times 13{\cdot}6 \times 980 \times 6{\cdot}023 \times 10^{23} \times 10^{6}}{8{\cdot}31 \times 10^{7} \times 273}$$

$$x = 2{\cdot}688 \times 10^{25}$$

Example 5·10 *Calculate the number of molecules in one litre of an ideal gas at 136·5°C temperature and 3 armospheres pressure.*

Let the number of molecules per cc $= n$

$$n = \frac{PN}{RT}$$

Number of molecules in one litre,

$$x = n \times 10^{3}$$

$$x = \frac{PN \times 10^{3}}{RT}$$

Here

$$P = 3 \times 76 \times 13{\cdot}6 \times 980 \ \text{dynes/cm}^{2}$$

$$N = 6{\cdot}023 \times 10^{23}$$

$$R = 8{\cdot}31 \times 10^{7} \ \text{ergs/g mol-K}$$

$$T = (273 + 136{\cdot}5)$$

$$= 409{\cdot}5 \text{ K}$$

$$\therefore \quad x = \frac{3 \times 76 \times 13{\cdot}6 \times 980 \times 6{\cdot}023 \times 10^{23} \times 10^{3}}{8{\cdot}31 \times 10^{7} \times 409{\cdot}5}$$

$$x = 5{\cdot}376 \times 10^{22}$$

Example 5·11 *The number of molecules per* cc *of a gas is* $2{\cdot}7 \times 10^{19}$ *at* N.T.P. *Calculate the number of molecules per* cc *of the gas.*

(*i*) *at 0°*C *and* 10^{-6} mm *pressure of mercury and*

(*ii*) *at 39°*C *and* 10^{-6} mm *pressure mercury.*

For a unit volume of a gas

$$P = \frac{1}{3} mnC^{2}$$

(*i*) At 0°C, R.M.S. velocity is equal to C

At N.T.P.

$$P_1 = \frac{1}{3} mn_1 C^{2} \qquad \ldots(i)$$

At 0°C and 10^{-6} mm pressure

$$P_2 = \frac{1}{3} mn_2 C^{2} \qquad \ldots(ii)$$

From (*i*) and (*ii*)

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

or

$$n_2 = \frac{n_1 \times P_2}{P_1}$$

Here
$$n_1 = 2{\cdot}7 \times 10^{19}$$
$$P_1 = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$P_2 = 10^{-6} \text{ mm of Hg}$$
$$= 10^{-7} \text{ cm of Hg}$$
$$P_2 = 10^{-7} \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$n_2 = \frac{2{\cdot}7 \times 10^{19} \times 10^{-7} \times 13{\cdot}6 \times 980}{76 \times 13{\cdot}6 \times 980}$$
$$n_2 = \mathbf{3{\cdot}553 \times 10^{10}}$$

(*ii*) Let the R.M.S. velocity at 0°C be C_2 and at 39°C be C_3. Number of molecules per cc at 0°C and 10^{-6} mm of Hg pressure

$$= n_2$$

and at 39°C and 10^{-6} mm of Hg pressure

$$= n_3$$

$$P = \frac{1}{3} mnC^2$$

Here pressure is the same in both the cases

$$\therefore \quad \frac{1}{3} mn_2C_2^2 = \frac{1}{3} mn_3C_3^2$$
$$\therefore \quad n_2C_2^2 = n_3C_3^2$$
$$n_3 = n_2 \frac{C_2^2}{C_3^2}$$

But
$$C \propto \sqrt{T}$$
$$\therefore \quad \frac{C_2^2}{C_3^2} = \frac{T_2}{T_3}$$
$$\therefore \quad n_3 = \frac{n_2 \times T_2}{T_3}$$

Here
$$n_2 = 3{\cdot}553 \times 10^{10}$$
$$T_2 = 0^\circ \text{ C}$$
$$= 273 \text{ K}$$
$$T_3 = 39^\circ \text{ C}$$
$$= 273 + 39$$
$$= 312 \text{ K}$$
$$\therefore \quad n_3 = \frac{3{\cdot}553 \times 10^{10} \times 273}{312}$$
$$n_3 = \mathbf{3{\cdot}109 \times 10^{10}}$$

5·19 Avogadro's Hypothesis

Consider two gases A and B at a pressure P and each having a volume V.

Mass of each molecule of the first gas $= m_1$

Number of molecules of the first gas $= n_1$

Mean square velocity of the molecules of the first gas = C_1^2

For the first gas

$$P = \frac{1}{3} \rho_1 C_1^2$$

$$= \frac{1}{3} \frac{m_1 n_1 C_1^2}{V} \qquad \ldots(i)$$

Similarly for the second gas

$$P = \frac{1}{3} \rho_2 C_2^2$$

$$= \frac{1}{3} \frac{m_2 n_2 C_2^2}{V} \qquad \ldots(ii)$$

where m_2 represents the mass of each molecule, n_2 the number of molecules and C_2^2 the mean square velocity of the molecules.

From (i) and (ii),

$$\frac{1}{3} \frac{m_1 n_1 C_1^2}{V} = \frac{1}{3} \frac{m_2 n_2 C_2^2}{V}$$

or

$$m_1 n_1 C_1^2 = m_2 n_2 C_2^2 \qquad \ldots(iii)$$

If the two gases are at the same temperature T, the mean kinetic energy of the molecules of both the gases is the same

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2$$

$$\therefore \quad m_1 C_1^2 = m_2 C_2^2 \qquad \ldots(iv)$$

From (iii) and (iv),

$$n_1 = n_2$$

Hence, equal volumes of all gases under similar conditions of temperature and pressure have the same number of molecules. This represents Avogadro's hypothesis.

5·20 Graham's Law of Diffusion of Gases

According to the kinetic theory

$$P = \frac{1}{3} \rho C^2$$

or

$$C = \sqrt{\frac{3P}{\rho}}$$

$$C \propto \frac{1}{\sqrt{\rho}}$$

It means that the root mean square velocity of the molecules of a gas is inversely proportional to the square root of its density. Consider two gases whose root mean square velocities are C_1 and C_2.

$$\frac{C_1}{C_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

or

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

Here, r_1 and r_2 represent the rates of diffusion of the two gases.

Example 5·12. *Calculate the total random kinetic energy of one gm-molecule of oxygen at 300* K.

Total random kinetic energy per gram-molecule of oxygen

$$
\begin{aligned}
&= \frac{1}{2}\, mC^2 \times N \\
&= \frac{3}{2}\, k\,T.N \\
&= \frac{3}{2} \cdot \frac{R}{N}\, T.N \\
&= \frac{3}{2} RT \\
&= \frac{3}{2} \times 8{\cdot}3 \times 10^7 \times 300 \\
&= 3{\cdot}735 \times 10^{10} \text{ ergs} \\
&= \textbf{3735 joules}
\end{aligned}
$$

Note. The total random kinetic energy for one gram-molecule of any gas *i.e.*, hydrogen, oxygen, helium, nitrogen, air etc. is the same at the same temperature.

Example 5·13. *Calculate the average kinetic energy of a molecule of a gas at a temperature of 300* K.

Average K.E. of a molecule

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

Here k is Boltzmann's constant

$$k = 1{\cdot}38 \times 10^{-16} \text{ erg/molecule-deg}$$

Average K.E. of a molecule $= \frac{3}{2} \times 1{\cdot}38 \times 10^{-16} \times 300$

$$= \mathbf{6{\cdot}21 \times 10^{-14}} \textbf{ ergs}$$

Note. The average kinetic energy of a molecule of any gas *i.e.*, hydrogen, oxygen, helium, nitrogen, air, etc., is the same at the same temperature.

Example 5·14. *Calculate the mean translational kinetic energy per molecule of a gas at 727°C, given R = 8·32* joules/mole-K

(*Delhi, 1974*)

Avogadro's number,

$$N = 6{\cdot}06 \times 10^{23}$$

Here

$$
\begin{aligned}
T &= 627 + 273 = 1000 \text{ K} \\
R &= 8{\cdot}32 \text{ joules/mol-K} \\
N &= 6{\cdot}06 \times 10^{23}
\end{aligned}
$$

$$k = \frac{R}{N} = \left(\frac{8{\cdot}32}{6{\cdot}06 \times 10^{23}}\right) \text{ joules/molecule-K}$$

Mean translational kinetic energy per molecule $= \frac{3}{2}\, kT$

$$= \frac{3\times 8{\cdot}32\times 1000}{2\times 6{\cdot}06\times 10^{23}}$$

$$= \mathbf{2{\cdot}059\times 10^{-20}\ joule}$$

Example 5·15. *Calculate the total random kinetic energy of one gram of nitrogen at 300* K.

Total random energy for one gram molecule of nitrogen

$$= \frac{3}{2}RT$$

Total random energy for 1 gram of nitrogen

$$= \frac{3}{2}\frac{RT}{M}$$

where the molecular weight of nitrogen $M = 28$ g

$$E = \frac{3RT}{2M}$$

$$= \frac{3\times 8{\cdot}3\times 10^7\times 300}{2\times 28}$$

$$= 133{\cdot}4\times 10^7 \text{ ergs}$$

$$= \mathbf{133{\cdot}4\ joule}$$

Note. The total random kinetic energy for 1 gram of a gas is different for different gases at the same temperature.

Example 5·16. *Calculate the total random kinetic energy of 2* g *of helium at 200* K.

Energy for 1 g of helium

$$= \frac{3RT}{2M}$$

Energy for 2 g of helium

$$= \frac{2\times 3\times RT}{2M}$$

$$= \frac{3RT}{M}$$

$$= \frac{3\times 8{\cdot}3\times 10^7\times 200}{4}$$

$$= 1245\times 10^7 \text{ ergs}$$

$$= \mathbf{1245\ joules}$$

Example 5·17. *Calculate the root mean square velocity of a molecule of mercury vapour at 300* K.

Mean kinetic energy of one molecule of mercury

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

Let N be the Avogadro's number.

Then $$\frac{1}{2}\, mNC^2 = \frac{3}{2}\, kNT$$

$$\frac{1}{2}\, MC^2 = \frac{3}{2} RT$$

$$C = \sqrt{\frac{3RT}{M}}$$

Here the molecular weight of mercury, $M = 221$

$$\therefore \qquad C = \sqrt{\frac{3\times 8{\cdot}3\times 10^7\times 300}{221}}$$

$$= \mathbf{1{\cdot}93\times 10^4\ cm/s}$$

Example 5 18 *With what speed would one gram molecule of oxygen at 300* K *be moving in order that the translational kinetic enegry of its centre of mass is equal to the total random kinetic energy of all its molecules ? Molecular weight of oxygen* (M) = *32.*

Total random kinetic energy of 1 gram-molecule of oxygen

$$= \frac{3}{2}\, RT = \frac{3}{2}\times 8{\cdot}3\times 10^7\times 300$$

$$= 3{\cdot}735\times 10^{10} \text{ ergs}$$

Kinetic energy of M grams of oxygen moving with a velocity v

$$= \frac{1}{2}\, Mv^2$$

$$\therefore \qquad \frac{1}{2} Mv^2 = 3{\cdot}735\times 10^{10}$$

$$\frac{1}{2}\times 32\times v^2 = 3{\cdot}735\times 10^{10}$$

$$v^2 = \frac{3{\cdot}735\times 10^{10}}{16}$$

$$\mathbf{x = 4{\cdot}8\times 10^4\ cm/s}$$

Example 5·19. *Calculate the temperature at which the r.m.s. velocity of a hydrogen molecule will be equal to the speed of the earth's first satellite* (*i.e.* $v = 8$ km/s).

Energy for 1 gram molecule of hydrogen

$$= \frac{1}{2}\, Mv^2 = \frac{3}{2}\, RT$$

$$T = \frac{Mv^2}{3R}$$

$$= \frac{2\times (8\times 10^5)^2}{3\times 8{\cdot}3\times 10^7}$$

$$= \mathbf{5{\cdot}14\times 10^3\ K}$$

Example 5·20. *At what temperature, pressure remaining constant, will the r.m.s. velocity of a gas be half its value at 0°*C ?

[*Delhi* (*Hons.*) *1975*]

$$\frac{C_2}{C_1} = \sqrt{\frac{T_2}{T_1}}$$

Here $C_2 = \frac{C_1}{2}$

$T_2 = ?$

$T_1 = 273$ K

$$\therefore \quad \frac{1}{2} = \sqrt{\frac{T_2}{273}}$$

$$\frac{1}{4} = \frac{T_2}{273}$$

$$T_2 = \frac{273}{4} = \mathbf{68{\cdot}25\ K}$$

or $T_2 = -204{\cdot}75°\text{C}$

5·21 Degrees of Freedom and Maxwell's Law of Equipartition of Energy

A molecule in a gas can move along any of the three co-ordinate axes. It has three degrees of freedom. Degrees of freedom mean the number of independent variables that must be known to describe the state or the position of the body completely. A monoatomic gas molecule has three degrees of freedom. A diatomic gas molecule has three degrees of freedom of translation and two degrees of freedom of rotation. It has in all five degrees of freedom.

According to kinetic theory of gases, the mean kinetic energy of a molecule at a temperature T is given by

$$\frac{1}{2}mC^2 = \frac{3}{2}kT \qquad \ldots(i)$$

But $C^2 = u^2+v^2+w^2$

As x, y and z are all equivalent, mean square velocities along the three axes are equal

$$\therefore \quad u^2 = v^2 = w^2$$

or $\frac{1}{2}m(u^2) = \frac{1}{2}m(v^2) = \frac{1}{2}m(w^2)$

$$\therefore \quad \tfrac{1}{2}mC^2 = 3\left[\tfrac{1}{2}m(u^2)\right] = 3\left[\tfrac{1}{2}m(v^2)\right]$$

$$= 3\left[\tfrac{1}{2}m(w^2)\right]$$

$$= \frac{3}{2}kT$$

$$\therefore \quad \tfrac{1}{2}mu^2 = \tfrac{1}{2}kT \qquad \ldots(ii)$$

$$\tfrac{1}{2}mv^2 = \tfrac{1}{2}kT \qquad \ldots(iii)$$

$$\tfrac{1}{2}mw^2 = \tfrac{1}{2}kT \qquad \ldots(iv)$$

Therefore, the average kinetic energy associated with each degree of freedom $= \frac{1}{2}kT$

Thus the energy associated with each degree of freedom (whether translatory or rotatory) is $\frac{1}{2}kT$.

This represents the theorem of equipartition of energy.

5·22 Atomicity of Gases

(*i*) *Mono atomic gas* A mono atomic gas molecule has one atom. Each molecule has three degrees of freedom due to translatory motion only.

Energy associated with each degree of freedom $= \frac{1}{2} kT$

Energy associated with three degrees of freedom

$$= \frac{3}{2} kT$$

Consider one gram molecule of a gas.

Energy associated with one gram molecule of a gas

$$= N \times \frac{3}{2} kT$$

$$= \frac{3}{2} (N \times k) T$$

[But, $N \times k = R$]

$$\therefore \quad U = \frac{3}{2} RT$$

This energy of the gas is due to the energy of its molecules. It is called internal energy U. For an ideal gas, it depends upon temperature only.

$$\therefore \quad C_v = \frac{dU}{dT} = \frac{3}{2} R$$

$\left(\frac{dU}{dT}\right.$ is the increase in internal energy per unit degree rise of temperature$\left.\right)$

But $\quad C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{3}{2} R + R = \frac{5}{2} R$$

For a mono-atomic gas

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{\frac{5}{2} R}{\frac{3}{2} R} = 1{\cdot}67$$

The value of γ is found to be true experimentally for monoatomic gases like argon and helium.

(*ii*) ***Diatomic gas.*** A diatomic gas molecule has two atoms. Such a molecule has three degrees of freedom of translation and two degrees of freedom of rotation.

Energy associated with each degree of freedom

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

Energy associated with 5 degrees of freedom $= \frac{5}{2} kT$

Consider one gram molecule of gas.

Energy associated with 1 gram molecule of a diatomic gas

$$= N \times \frac{5}{2} kT = \frac{5}{2} RT$$

$$U = \frac{5}{2} RT$$

$$C_V = \frac{dU}{dT}$$

$$= \frac{5}{2} R$$

But
$$C_P - C_V = R$$
$$C_P = C_V + R$$
$$= \frac{5}{2} R + R = 7/2\ R$$
$$\gamma = \frac{C_P}{C_V}$$
$$= \frac{\frac{7}{2} R}{\frac{5}{2} R} = 1{\cdot}40$$

The value of $\gamma = 1{\cdot}40$ has been found to be true experimentally for diatomic gases like hydrogen, oxygen, nitrogen etc.

(*iii*) ***Triatomic gas.*** (*a*) A triatomic gas having 6 degrees of freedom has an energy associated with 1 gram molecule

$$= N \times \frac{6}{2} kT = 3RT$$

$$U = 3RT$$

$$C_V = \frac{dU}{dT} = 3R$$

But
$$C_P - C_V = R$$
$$C_P = C_V + R$$
$$= 3R + R = 4R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{4R}{3R} = 1{\cdot}33$$

(*b*) A triatomic gas having 7 degrees of freedom has an energy associated with 1 gram molecule $= N \times \frac{7}{2}\, kT = \frac{7}{2} R$

$$U = \frac{7}{2}\, RT$$

$$C_V = \frac{dU}{dT} = \frac{7}{2} R$$

But $$C_P - C_V = R$$

$$C_P = C_V + R$$

$$= \frac{7}{2} R + R = \frac{9}{2} R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{9/2\, R}{7/2\, R} = 1{\cdot}28$$

Thus the value of γ, C_P and C_V can be calculated depending upon the degrees of freedom of a gas molecule.

5·23 Maxwell's Law of Distribution of Velocity

At a particular temperature, a gas molecule has a fixed mean kinetic energy. It does not mean that the molecule is moving with the same speed throughout its movement. After each encounter the speed of the molecule changes and due to a large number of collisions, the speed is different at different instants. But the root mean square velocity (r.m s.) C remains the same at a fixed temperature. At any instant, all the molecules are not moving with the same velocity. Some are moving with a velocity higher than C and the others with a velocity lower than C But the mean kinetic energy of all the molecules remains constant at a given temperature.

Derivation of Maxwell's law of Distribution of Molecular velocities

The mean square velocity of molecules is defined by the equation

$$C^2 = \frac{1}{N} \int_0^\infty c^2\, dN$$

Here dN is the number of molecules having velocities between c and $c+dc$. If the total number of molecules is N, then a fraction $\frac{dN}{N}$ will have the components of velocities in x direction in the range

u and $u+du$. However, the fraction $\frac{dN_x}{N}$ is a function of U only and is proportional to du.

$$\therefore \qquad \frac{dN_x}{N} = f(u)du$$

$$\therefore \qquad dN_x = N\,f(u)\,du$$

The equations for y and z directions are

$$dN_y = Nf(v)dv$$

and
$$dN_z = Nf(w)dw$$

Also the value of N is too large and du is small compared with u but in range u and $u+du$, there are a large number of molecules. The fraction of dN_x molecules whose y components of velocity lie in the range v and $v+dv$ is given by the equation

$$\frac{d^2N_{x,y}}{dN_x} = \frac{dN_y}{N} = f(v)dv$$

$$\therefore \qquad d^2N_{x,y} = N\,f(u)\,f(v)du\,dv$$

The number of molecules represented by $d^2N_{x,y}$ is still large Suppose that the fraction of these molecules $d^2N_{x,y}$, whose components of velocity in Z direction in the range w and $w+dw$ is given by the equation

$$d^3N_{x,y,z} = Nf(u)\,f(v)\,f(w)du\,dv\,dw$$

The density of velocity points is given by the equation

$$\rho = \frac{d^3N_{x,y,z}}{du\,dv\,dw} = Nf(u)\,f(v)\,f(w)$$

As there is no preferred direction of the velocities, the density of velocity points ρ is constant *i.e.*, velocity space is isotropic.

Also
$$U^2 = u^2+v^2+w^2$$

$$\therefore \qquad Nf(u)\,f(v)\,f(w) = \text{const.} \qquad \ldots(i)$$

when
$$u^2+v^2+w^2 = \text{constant} \qquad \ldots(ii)$$

These equations (*i*) and (*ii*) must be simultaneously satisfied. Equation (*ii*) limits the values of the variables in equation (*i*) and reduces the number of independent variables to two. Therefore it is called an equation of constraint.

Differentiating equations (*i*) and (*ii*)

$$f(v)\,f(w)\,\frac{\partial f(u)}{\partial u}\,du + f(w)\,f(u)\,\frac{\partial f(v)}{\partial v}\,dv$$
$$+ f(u)\,f(v)\,\frac{\partial f(w)}{\partial w}\,dw = 0 \qquad \ldots(iii)$$

and
$$2u\,du + 2v\,dv + 2w\,dw = 0 \qquad \ldots(iv)$$

Simplifying equations (*iii*) and (*iv*)

$$\frac{1}{f(u)}\frac{\partial f(u)}{\partial u}du+\frac{1}{f(v)}\frac{\partial f(v)}{\partial v}dv$$

$$+\frac{1}{f(w)}\frac{\partial f(w)}{\partial w}dw=0 \qquad \ldots(v)$$

and

$$u\,du+v\,dv+w\,dw=0 \qquad \ldots(vi)$$

As there are only two independent variables, arbitrary values cannot be given to all the three differentials. Suppose the arbitrary values are given to *dv* and *dw*. Multiply equation (*vi*) by $m\beta$ where *m* is the mass of the molecules and β is an arbitrary, unknown function. The product $m\beta$ is called Langrange undetermined multiplier.

$$\therefore \qquad m\beta[u\,du+v\,dv+w\,dw]=0 \qquad \ldots(vii)$$

Adding equations (*v*) and (*vii*)

$$\left[\frac{1}{f(u)}\frac{\partial f(u)}{\partial u}+m\beta u\right]du+\left[\frac{1}{f(v)}\frac{\partial f(v)}{\partial v}+m\beta v\right]dv$$

$$+\left[\frac{1}{f(w)}\frac{\partial f(w)}{\partial w}+m\beta w\right]dw=0 \qquad \ldots(viii)$$

As the two variables *v* and *w* are considered to be independent, their differentials are arbitrary and the values, $dv=0$ and $dw=0$ may be assigned to them.

From equation (*viii*)

$$\left(\frac{1}{f(u)}\frac{\partial f(u)}{\partial u}+m\beta u\right)=0 \qquad \ldots(ix)$$

Taking $dv=0$, and $dw\neq 0$, we get

$$\frac{1}{f(w)}\frac{\partial f(w)}{\partial w}+m\beta w=0 \qquad \ldots(x)$$

Taking $dw=0$ and $dv\neq 0$

$$\frac{1}{f(v)}\frac{\partial f(v)}{\partial v}+m\beta v=0 \qquad \ldots(xi)$$

To satisfy equations (*ix*), (*x*) and (*xi*), β would either be a constant or a function of the variable in that equation. A constant value of β is the only value that can satisfy all the equations. It is clear from the above equations that the function *f* satisfies the same differential equation irrespective of the component.

For the *x* component

$$\frac{d}{du}[\log f(u)]=-m\beta u$$

$$\int d[\log f(u)]=-m\beta\int u\,du$$

$$\log f(u)=-\beta(\tfrac{1}{2}mu^2)+\log A \qquad \ldots(xii)$$

Here *A* is a constant of integration.

From equation (*xii*)

$$f(u) = Ae^{-\beta(\frac{1}{2}mu^2)} \qquad \ldots(xiii)$$

Similarly

$$f(v) = Ae^{-\beta(\frac{1}{2}mv^2)} \qquad \ldots(xiv)$$

and

$$f(w) = Ae^{-\beta(\frac{1}{2}mw^2)} \qquad \ldots(xv)$$

From these three equations, the density of velocity points is given by

$$\rho = NA^3e^{-\beta[\frac{1}{2}m(u^2+v^2+w^2)]}$$

or

$$\rho = NA^3\, e^{-\beta[\frac{1}{2}mc^2]} \qquad \ldots(xvi)$$

But

$$\rho = \frac{d^3N_{x,\,y,\,z}}{du\;dv\;dw} \qquad \ldots(xvii)$$

i.e. the number of molecules with components of velocity lying in a small cubical volume divided by the volume element. However ρ is constant within the infinitesimal spherical shell within the radii c and $c+dc$. The volume of this element is $4\pi c^2dc$. This volume element contains dN molecules.

$$\therefore \qquad \rho = \frac{dN}{4\pi c^2\, dc} \qquad \ldots(xviii)$$

From equations (*xvi*) and (*xviii*)

$$\frac{dN}{4\pi c^2dc} = NA^3\; e^{-\beta[\frac{1}{2}mc^2]}$$

or

$$\frac{dN}{dc} = 4\pi NA^3c^2e^{-\beta[\frac{1}{2}mc^2]} \qquad \ldots(xix)$$

$$\therefore \qquad dN = 4\pi NA^3\; e^{-bc^2}\, c^2dc \qquad \ldots(xx)$$

where N represents the number of molecules per cc and

$$A = \sqrt{\frac{b}{\pi}} \text{ and } b = \frac{\beta m}{2}$$

and

$$b = \frac{m}{2kT},\; \beta = \frac{1}{kT}$$

Here k is Boltzmann's constant.

The graph representing dN/dc and speed is shown in Fig. 5·8.

The shaded area in the figure represents the number of molecules dN having velocities between c and $c+dc$. The number of molecules possessing the root mean square velocity C is maximum.

The number of molecules having very low or very high velocity is small. The total area under the curve represents the tolal number of molecules.

From equation (*xx*)

$$\frac{dN}{dc} = 4\pi N\left[\frac{m}{2\pi kT}\right]^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$

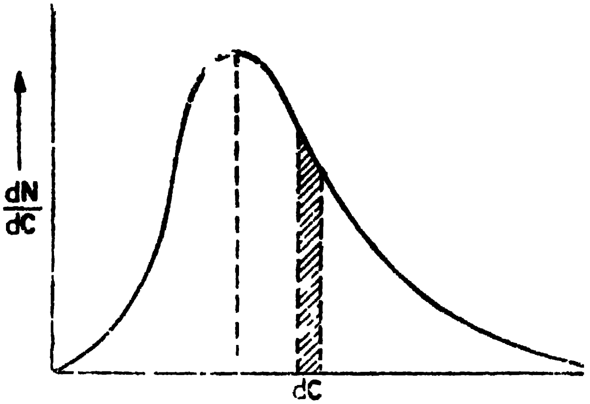


Fig. 5·8

$$\frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}} \qquad \ldots(xxi)$$

Taking $\frac{1}{2}mc^2 = E$ where E is the mean kinetic energy of a molecule,

$$\frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} c^2 e^{-\frac{E}{kT}} \qquad \ldots(xxii)$$

Thus, Maxwell's law of distribution of velocities shows that the mean kinetic energy of all the molecules of a gas remains constant at a fixed temperature, though at any instant the molecules are moving with different velocities.

5·24 Experimental Verification of Velocity Distribution

Zartman and Ko (1934) performed an experiment to study the distribution of velocity. The apparatus consists of an oven with an opening at A. S_1 and S_2 are two parallel slits. A drum D can be rotated about an axis passing through O. P is a glass surface on which a beam of silver atoms will get deposited (Fig. 5·9).

Metallic silver is melted in the oven. A beam of silver atoms is ejected through A. The drum D is rotated with a speed of 6000 r.p.m. approximately. When the drum is stationary, the silver atoms get deposited at the same point on the glass plate. When the drum is rotated a fine beam of silver molecules enters through the slit S_2. Molecules with very high speeds reach the plate P first, *i.e.*, on the right end of P and molecules with very low speeds reach the other end of the plate. After a short time, sufficient quantity of silver is deposited on the plate P. Using a spectro-photometer, the relative intensity of silver on the plate P is studied and this represents the velocity distribution of the molecules. The graph representing the number of molecules and velocity agrees with Maxwell's distribution of velocity

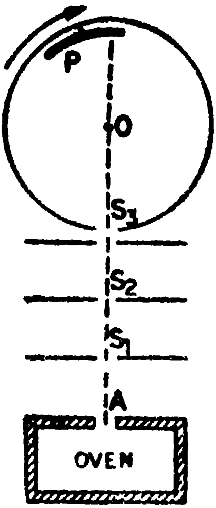


Fig. 5·9

In 1947, Estermann, Simpson and Stern designed a more precise apparatus to study the velocity distribution.

Cesium atoms from the oven emerge from the opening A (Fig. 5·10). S is a slit and D is a hot tungsten wire. The whole apparatus is enclosed in an evacuated chamber (pressure 10^{-8} mm of Hg). The opening A and the slit S are horizontal. In the absence of a gravitational field, cesium atoms will strike the wire at D. But due to the gravitational field, the path is a parabola. The atoms going along the path 3 do not reach the wire. The atoms going along the paths 1 and 2 reach at D_1 and D_2 respectively. The velocity of the atoms in path 1 is higher than the path 2.

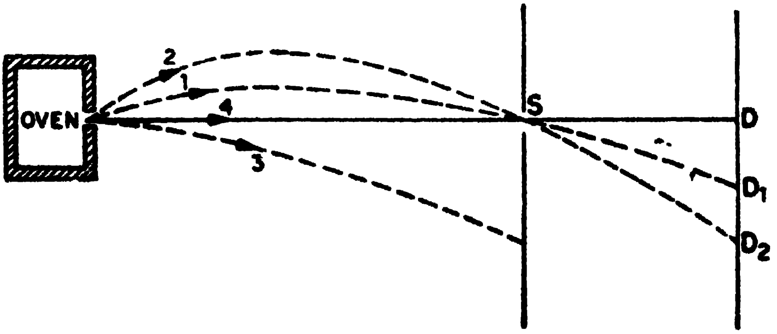


Fig. 5·10

When cesium atoms strike the wire they get ionized and re-evaporate. They are collected by a negatively charged detecting cylinder surrounding the tungsten wire. The magnitude of the current indicates the intensity of the atoms at various positions. The detector can be moved to different positions of the wire. The atoms reaching at D_1 have higher velocity than those reaching at D_2. The vertical height of the detector represents the magnitude of the velocity and the ionization current indicates the number of atoms striking the wire at a particular point. A graph is drawn between the ionization current along the y-axis and the vertical height (speed of the atoms) of the detector along the x axis. The velocity distribution is found to be in agreement with the Maxwellian distribution law of velocity.

5 25 Mean Free Path

In deriving the expression for the pressure of a gas on the basis of kinetic theory, it was assumed that the molecules are of negligible size. They were assumed to be geometrical points. A geometrical point has no dimensions and hence inter-molecular collisions will not be possible. But, a molecule has a finite size (though small) and moves in the space of the vessel containing it. It collides with other molecules and the walls of the containing vessel. The path covered by a molecule between any two consecutive collisions is a straight line, and is called the **free path**. The direction of the molecule is changed after every collision. After a number of collisions, the total path appears to be zig-zag and the free path is not constant (Fig. 5·11). Therefore, a term **mean free path** is used to indicate the mean distance travelled by a molecule between two collisions. If the total distance travelled after N collisions is S, then the mean free path λ is given by

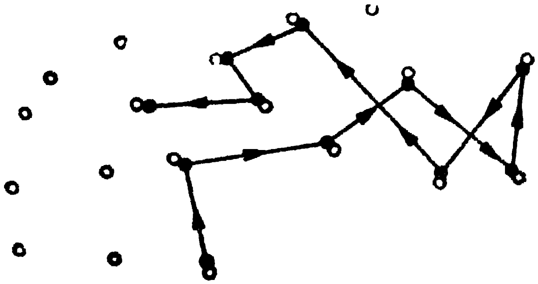


Fig. 5·11

$$\lambda = \frac{S}{N} \qquad \ldots(i)$$

Let the molecules be assumed to be spheres of diameter d. A collision between two molecules will take place if the distance between the centres of the two molecules is d. Collision will also occur if the colliding molecule has a diameter $2d$ and the other molecule is simply a geometrical point. Thus, assuming all other molecules to be geometrical points and the colliding molecule of diameter $2d$, this molecule will cover a volume $\pi d^2 v$ in one second. This corresponds to the volume of a cylinder of diameter $2d$ and length v.

Let n be the number of molecules per cc.

Then, the number of molecules present in a volume $\pi d^2 v$

$$= \pi d^2 v \times n$$

This value also represents the number of collisions made by the molecule in one second.

The distance moved in one second $= v$ and the number of collisions in one second $= \pi d^2 v \times n$.

$$\therefore \quad \text{Mean free path } \lambda = \frac{v}{\pi d^2 v n}$$

$$= \frac{1}{\pi d^2 n} \qquad \ldots(i)$$

This equation was deduced by Clausius.

$$\therefore \qquad \lambda \propto \frac{1}{d^2} \qquad \ldots(ii)$$

The mean free path is inversely proportional to the square of the diameter of the molecules.

Let m be the mass of each molecule.

Then, $m \times n = \rho$

$$\lambda = \frac{m}{\pi d^2 \rho} \qquad \ldots(iii)$$

The mean free path is inversely proportional to the density of the gas.

The expression for the mean path according to Boltzmann is

$$\lambda = \frac{3}{4\pi d^2 n} \qquad \ldots(iv)$$

He assumed that all molecules have the same average speed.

Maxwell derived the expression,

$$\lambda = \frac{1}{\sqrt{2}.\pi d^2 n} \qquad \ldots(v)$$

He calculated the value of λ on the basis of the law of distribution of velocities

TABLE

Mean Free Path (λ)

Gas	d	λ
Hydrogen	$2{\cdot}47 \times 10^{-8}$ cm	$1{\cdot}83 \times 10^{-5}$ cm
Nitrogen	$3{\cdot}50 \times 10^{-8}$ cm	$0{\cdot}944 \times 10^{-5}$ cm
Helium	$2{\cdot}18 \times 10^{-8}$ cm	$2{\cdot}85 \times 10^{-5}$ cm
Oxygen	$3{\cdot}39 \times 10^{-8}$ cm	$0{\cdot}999 \times 10^{-5}$ cm

Determination of mean free path. As discussed in article 5·27, the relation between coefficient of viscosity and the mean free path of a molecule is given by

$$\eta = \frac{1}{3} mnC\lambda$$

For unit volume,

$$mn = \rho$$

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

$$\lambda = \frac{3\eta}{\rho C} \qquad \ldots(i)$$

The root mean square velocity C of a molecule can be calculated knowing pressure, density and temperature. The coefficient of viscosity of the gas is determined experimentally. Hence the value of the mean free path of a molecule can be calculated from equation (*i*).

5·26 Transport Phenomena

According to Maxwell's law of distribution of velocity

$$dN = 4\pi NA^3 e^{-bc^2} c^2 dc \qquad \ldots(i)$$

But

$$4\pi c^2 dc = du\,dv\,dw$$

$$dN = NA^3 e^{-bc^2} du\,dv\,dw \qquad \ldots(ii)$$

Also

$$c^2 = u^2+v^2+w^2$$

$$\therefore \qquad dN = NA^3 e^{-b(u^2+v^2+w^2)} du\,dv\,dw \qquad \ldots(iii)$$

Equation (*iii*) has to be modified in case the gas as a whole possesses mass motion.

Let u_0, v_0 and w_0 be the components of the mass velocity. Therefore, the actual velocity of a molecule consists of two parts :

(*i*) the mass velocity components u_0, v_0 and w_0

(*ii*) the random thermal velocity components

$$u-u_0,\ v-v_0 \text{ and } w-w_0$$

Corresponding to thermal motion without mass motion, similar quantities with mass motion are

$$U = u-u_0$$

$$V = v-v_0$$

and

$$W = w-w_0$$

From equation (*iii*), Maxwell's law of distribution of velocity can be written as

$$dN = NA^3 e^{-b(U^2+V^2+W^2)} dU\,dV\,dW \ldots(iv)$$

Equation (*iv*) holds good only if u_0, v_0, w_0, T and N are constant throughout the gas.

If the gas is not in an equilibrium state, there are three possibilities occurring singly or jointly.

(1) The components of velocity, u_0, v_0, and w_0 may not have the same value in all parts of the gas. This will result in relative motion of the gas layers with respect to one another.

There is relative velocity between different layers of the gas. This gives rise to the phenomena of viscosity.

(2) The temperature of the gas may not be the same throughout. This results in the transference of thermal energy from regions of higher to lower temperature. This gives rise to the phenomenon of conduction.

(3) The number of molecules per cc *i.e.*, N, may not be the same throughout the volume of the gas. This results in the movement of molecules from regions of higher value of N to lower value of N. This gives rise to the phenomenon of diffusion.

From the above disussion it is clear that the transport of momentum, energy and mass represent viscosity, conduction and diffusion respectively These are called *transport phenomena.* From the thermodynamic point of view, the transport phenomena are irreversible.

The transport phenomena occur due to the thermal agitation of the molecules The molecules in a particular layer are associated with certain values of velocity components, temperature and molecular density. They tend to minimise the differences in u_0, v_0, w_0, T and N. The molecules actually possess large velocities, whereas these phenomena of viscosity, conduction and diffusion are comparatively slow. This anomaly is explained on the fact that the molecules frequently collide. Therefore the transport phenomena are basically governed by the mean free path λ of a molecule. *A molecule moving through a free path λ is actually transferring momentum, energy and mass through a distance λ.*

The transport phenomena occur only in the non-equilibrium state of a gas.

5·27 Viscosity of Gases

Consider a gas flowing along a horizontal surface. The layer in contact with the wall of the surface is at rest. The velocity of the layer increases with increase in distance from the fixed layer.

Viscosity is defined as the tangential force per unit area required to maintain a unit velocity gradient.

$$F = -\eta A \frac{du}{dx} \qquad .(i)$$

Here η is the coefficient of viscosity and A is the area of the layer and $\frac{du}{dx}$ is the velocity gradient.

The velocity of a molecule at any layer at a height x above the fixed layer $= x \times \frac{du}{dx}$. If the mean free path of a molecule is

λ, then the distance for the first collision to occur $= (x-\lambda)$. The average velocity of these molecules $= (x-\lambda)\dfrac{du}{dx}$.

The molecules are moving at random in all directions. Approximately it can be assumed that about one-third of the molecules are moving along each axis. As the molecules in a given space will be free to move in any direction, one-sixth can be assumed to be moving in one direction and the other one-sixth in the opposite direction.

Let C be the r.m.s. velocity of the molecules, n the number of molecules per cc and m the mass of each molecule. Then, the number of molecules crossing unit area in one direction in one second $= \dfrac{1}{6}\, nC$.

Mass of the molecules $= \dfrac{1}{6}\, mnC = M$

Momentum in the forward direction

$$= M\left[(x-\lambda)\frac{du}{dx}\right]$$

Momentum in the opposite direction

$$= M\left[\{x-(-\lambda)\}\frac{du}{dx}\right]$$

Total change in momentum in one second

$$F = M(x-\lambda)\frac{du}{dx} - M(x+\lambda)\frac{du}{dx}$$

$$F = -2\,M\,\lambda\,\frac{du}{dr}$$

$$F = -2\left[\frac{1}{6}\, mnC\right]\lambda\,\frac{du}{dx}$$

$$= -\frac{1}{3}\, mnC\,\lambda\,\frac{du}{dx} \qquad \ldots(ii)$$

Comparing (i) and (ii)

$$\eta A\frac{du}{dx} = \frac{1}{3}\, mnC\,\lambda\,\frac{du}{dx}$$

But $\qquad A = 1$ sq cm

$\therefore$
$$\eta = \frac{1}{3}\, mnC\lambda \qquad \ldots(iii)$$

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

$$\eta = \frac{1}{3}\, mnC\,\frac{1}{\sqrt{2}\,\pi\,\sigma^2 n}$$

$$\eta = \frac{mC}{3\sqrt{2}\,\pi\sigma^2} \qquad \ldots(iv)$$

But $$C \propto \sqrt{T}$$

$$\therefore \quad \eta \propto \sqrt{T} \qquad ...(v)$$

The coefficient of viscosity of a gas is directly proportional to the square root of its temperature in K.

5·28 Thermal Conductivity of Gases

The thermal conductivity of gases can be explained on the basis of kinetic theory of gases. The gas molecules are free to move between the hot end and the cold end. They are also free to move in any direction. Let the temperature gradient be $\frac{d\theta}{dx}$ and the mean free path λ. The temperature decreases from the hot to the cold end and when the steady state is reached, the temperature gradient will be uniform.

The mean temperature of the molecules crossing the layer P from the cold side $= \left(\theta - \frac{d\theta}{dx}\lambda\right)$ and the mean temperature of the molecules crossing the layer P from the hot end $= \left(\theta + \frac{d\theta}{dx}\lambda\right)$.

Let n be the number of molecules per cc, m the mass of each molecule and C the r.m.s. velocity of the molecules. On the average only $\frac{1}{6}$ of the molecules will be moving from the hot to the cold end and $\frac{1}{6}$ of the molecules will be moving from the cold to the hot end. Consider one sq cm area of cross-section at the layer P (Fig. 5·12).

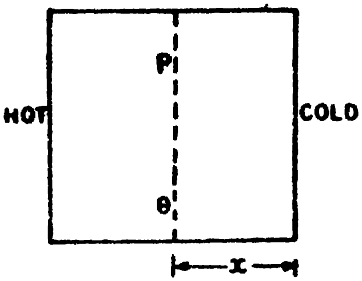


Fig. 5·12

The mass of the molecules crossing a unit area of cross-section in one second

$$= \frac{1}{6} mnC = M$$

$\therefore$ Heat energy carried by the molecules crossing the unit area of the layer in one second from the hot to the cold end

$$= MC_v\left(\theta + \frac{d\theta}{dx}\cdot\lambda\right)$$

Heat carried by the molecules crossing the area of the layer in one second from the cold to the hot end

$$= MC_v\left(\theta - \frac{d\theta}{dx}\lambda\right)$$

Therefore, the net heat conducted per unit area per second from the hot to the cold end

$$H = MC_v\left[\theta + \frac{d\theta}{dx}\lambda\right] - MC_v\left[\theta - \frac{d\theta}{dx}\lambda\right]$$

$$H = 2MC_v\lambda\frac{d\theta}{dx} \qquad ..(i)$$

$$\therefore \quad H = 2\left[\frac{1}{6}mnC\right]C_v\lambda\frac{d\theta}{dx}$$

$$H = \frac{1}{3}mnC.C_v\lambda\frac{d\theta}{dx} \qquad ...(ii)$$

From the definition of thermal conductivity

$$H = KA\,.\,\frac{d\theta}{dx}\,.\,t$$

Here $A = 1$ sq cm

$t = 1$ second

$$\therefore \quad H = K\,.\,\frac{d\theta}{dx} \qquad ...(iii)$$

Comparing (*ii*) and (*iii*)

$$K = \frac{1}{3}mnC\,C_v\lambda \qquad ...(iv)$$

$$K = \frac{1}{3}mnC\,.\,C_v \times \frac{1}{\sqrt{2}\,.\,\pi\sigma^2 n}$$

$$= \frac{mC.C_v}{3\sqrt{2}.\pi\sigma^2} \qquad ...(v)$$

But $C \propto \sqrt{T}$

$$\therefore \quad K \propto \sqrt{T}$$

The coefficient of thermal conductivity of a gas is directly proportional to the square root of the absolute temperature.

5 29 Atomic Heat of Solids

A solid is made up of a number of atoms. The atoms can be considered as elastic spheres vibrating about their mean positions. The atoms will have three degrees of freedom in a solid. The kinetic energy for each degree of freedom = $\frac{1}{2}kT$. But an atom has potential energy also. The mean potential energy is equal to the mean kinetic energy. Therefore, the total energy associated for each degree of freedom of an atom = $2 \times \frac{1}{2}kT$. The total energy associated for three degrees of freedom = $3kT$. The energy associated with 1 gram molecule

$$= N \times 3kT = 3RT$$

$$U = 3RT$$

$$A_H = \frac{dU}{dT}$$

$$= 3R = 5{\cdot}96 \text{ cals/g-mole K}$$

Thus, the atomic heat of solids (A_H) is $3R$ and this value agrees with the Dulong and Petit's Law.

Example 5·21. *In an experiment, the viscosity of the gas was found to be* $1{\cdot}66 \times 10^{-4}$ dynes/cm² *per unit velocity gradient. The R.M.S. velocity of the molecules is* $4{\cdot}5 \times 10^{4}$ cm/s. *The density of the gas is 1·25* grams *per* litre.

Calculate (i) the mean free path of the molecules of the gas, (ii) frequency of collision and (iii) molecular diameter of the gas molecules.

Here $\eta = 1{\cdot}66 \times 10^{-4}$ units

$$C = 4{\cdot}5 \times 10^{4} \text{ cm/s}$$

$$\rho = 1{\cdot}25 \times 10^{-3} \text{ g/cc}$$

(i)
$$\lambda = \frac{3\eta}{\rho C}$$

$$\lambda = \frac{3 \times 1{\cdot}66 \times 10^{-4}}{1{\cdot}25 \times 10^{-3} \times 4{\cdot}5 \times 10^{4}}$$

$$\lambda = 9 \times 10^{-6} \text{ cm}$$

(ii) Frequency of collision = number of collisions per second

$$= \frac{R.M.S. \text{ velocity}}{\text{Mean free path}}$$

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

$$N = \frac{4{\cdot}5 \times 10^{4}}{9 \times 10^{-6}}$$

$$N = 5 \times 10^{9}$$

(iii) Avogadro's number

$$= 6{\cdot}023 \times 10^{23}$$

Number of molecules per cc $= n$

$$= \frac{6{\cdot}023 \times 10^{23}}{22400}$$

According to Maxwell's relation

$$\lambda = \frac{1}{\sqrt{2} \, . \, \pi d^2 n}$$

$d = \frac{1}{\text{[illegible]}}$

$$d = \frac{1}{\sqrt{1.414\times 3.142\times\left(\frac{6.023\times 10^{23}}{22400}\right)\times 9\times 10^{\text{[illegible]}}}}$$

$$d = 3\times 10^{-8}\ \text{cm}$$

Example 5·22. *In an experiment the viscosity of a gas was found to be 2·25 × 10⁻⁴ CGS units. The RMS velocity of the molecules is 4·5 × 10⁴* cm/s. *The density of the gas is 1* gram *per* litre. *Calculate the mean free path of the molecules.*

Here

$$\eta = 2.25\times 10^{-4}\ \text{CGS units}$$

$$C = 4.5\times 10^{4}\ \text{cm/s}$$

$$\rho = 1\ \text{g/litre}$$

$$\therefore \quad \rho = 10^{-3}\ \text{g/cc}$$

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

$$\lambda = \frac{3\times 2.25\times 10^{-4}}{10^{-3}\times 4.5\times 10^{4}}$$

$$\lambda = 15\times 10^{-6}\ \text{cm}$$

Example 5·23 *Calculate the mean free path of a gas molecule, given that the molecular diameter is 2 × 10⁻⁸* cm *and the number of molecule per* cc *is 3 × 10¹⁹.*

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

$$= \frac{1}{3.14\times(2\times 10^{-8})^2\times 3\times 10^{19}}$$

$$\lambda = 3\times 10^{-5}\ \text{cm}$$

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

Example 5·24. *Calculate the mean free path of gas molecules in a chamber of 10⁻⁶* mm *of mercury pressure, assuming the molecular diameter to be 2Å. One gram molecule of the gas occupies 22·4* litres *at* N T P *Take the temperature of the chamber to be 273* K. *(Agra 1976)*

At 760 mm Hg pressure and 273 K temperature, the number of molecules in 22·4 litres of a gas

$$= 6.023\times 10^{23}$$

Therefore, the number of molecules per cm³ in the chamber at 10⁻⁶ mm pressure and 273 K temperature

$$n = \frac{6.023\times 10^{23}\times 10^{-6}}{22400\times 760}$$

$$n = 3.538\times 10^{10}\ \text{molecules/cm}^3$$

$$d = 2\text{Å} = 2\times 10^{-8}\ \text{cm}$$

Mean free path,

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

$$= \frac{1}{3.14\times(2\times 10^{-8})^2\times 3.538\times 10^{10}} = 2.25\times 10^{4}\ \text{cm}$$

5·30 Change of State

The molecules in a liquid have random motion. The average kinetic energy of the molecules depends upon the temperature. The molecules are held together to occupy a particular volume due to inter-molecular attraction.

Consider water kept in a tray and exposed to the atmosphere. Generally, the atmosphere is not saturated with water vapours. The molecules of the liquid which are in a state of constant random motion collide with each other resulting in exchange of kinetic energies. Thus, there exists the possibility of a particular molecule in the vicinity of water air interface acquiring sufficiently high kinetic energy. This energy of the molecule may be high enough to enable the molecule to break away from the forces of attraction of the surrounding molecules. In fact, a molecule on the interface experiences minimum force of attraction. Such a molecule goes into vapour state. When this molecule leaves the liquid, the mean kinetic energy of the remaining liquid molecules decreases and there is fall in temperature. This explains cooling caused by evaporation. Some vapour molecules in the atmosphere, also coalesce and get absorbed by the water surface. This is called condensation. Evaporation and condensation continue simultaneously but rate of evaporation is higher than the rate of condensation.

An important condition for cooling due to evaporation is the capacity of air to absorb more moisture.

If the liquid is heated, and if the rise in temperature of the liquid is more than the cooling caused by evaporation, the temperature of the liquid increases in addition to the increase in the rate of evaporation. A stage will come when the rate of heat supply is exactly equal to the energy needed for evaporation. At this stage evaporation takes place without change in temperature. This is boiling. At the boiling point the molecules are pulled further apart and their positions are no longer restricted to the space occupied by the liquid. This explains the change of state from liquid to gas or vapour. The amount of work done in pulling the molecules apart measures the latent heat of vaporisation. At the boiling point, the heat supplied to the liquid is used up only in pulling the molecules apart against the forces of intermolecular attraction and hence no rise in temperature of the liquid is noticed till the whole of the liquid is changed to the gaseous state. 1 cc of water when converted to steam occupies a volume of 1600 cc. This means that the mean inter-molecular distance is approximately 11·7 times more ($\sqrt[3]{1600} =$ 11·7 approximately) in a gas than the corresponding liquid.

5·31 Continuity of State

A substance can exist in three states *viz.*, solid, liquid and gas. For a long time it was supposed that gases like hydrogen, nitrogen, oxygen, helium etc. exist only in the gaseous form. It was also supposed that liquid and gaseous states are not continuous but are distinctly separate from one another. It was found that at high pressures and low temperatures, there are marked deviations from Boyle's law. At high pressure, the molecules of a gas come close to each other and the forces of inter-molecular attraction become appreciable. If these molecular distances become equal to those of the corresponding liquid, the gas gets liquefied.

The three states of a substance are continuous *i.e.*, solid, liquid and gaseous states are the three different stages of a continuous phenomenon. If ice is heated, its molecules become more free to move and it is converted to the liquid state (water). Further heating increases the molecular movement and when inter-molecular forces become small, at a particular stage it is converted into the gaseous state (steam). The reverse process is also possible by continuously withdrawing heat.

Faraday was able to liquefy chlorine under its own pressure with the help of a freezing mixture.

Cagniard de la Tour's Experiment

The apparatus consists of a tube having a bulb *B*. It contains mercury and above the surface of mercury in *B*, the bulb contains water or alcohol (Fig. 5·13). There is air at the top end of the tube *A*.

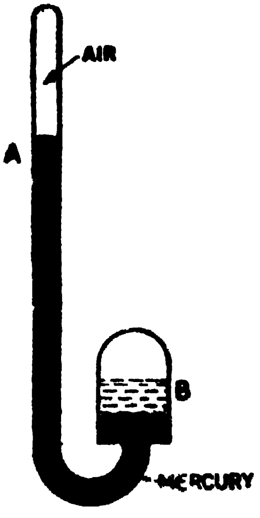


Fig. 5·13

The space above the liquid in the bulb *B* contains only the saturated vapours of the liquid at room temperature. The free surface of the liquid is visible and there is a marked distinction in the boundary of the liquid and its vapour. The bulb *B* is gradually heated. After some time the whole space in the bulb *B* appears foggy though the whole of the liquid has not evaporated. There is no free surface of the liquid at this stage. This shows that there is no distinction in the boundary of the liquid and the gaseous states.

When the bulb is allowed to cool, a cloud appears and it gets condensed. Again the free surface of the liquid is visible. This shows that there is a continuity between the liquid and the gaseous states of a substance. They are two different stages of a continuous phenomenon.

5·32 Andrews' Experiments on Carbon Dioxide

The apparatus used by Andrews to study the isothermals of carbon dioxide at various temperatures is shown in Fig. 5·14. *A* and *B*

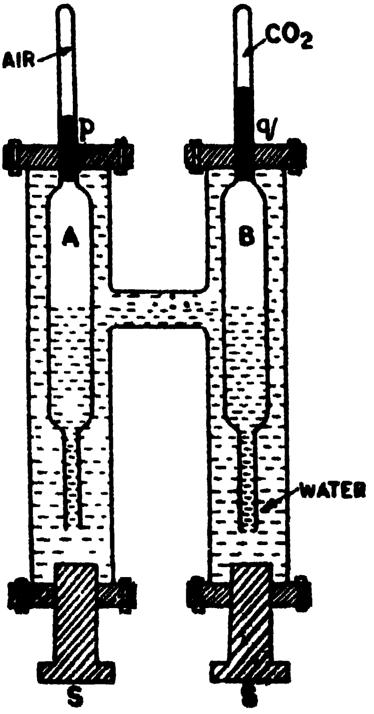


Fig. 5·14

are two similar glass tubes having thick capillary tubes at the top and bulbs in the middle. Initially in the tube *A* pure dry air is passed for a long time and it is sealed. In the bulb *B* carbon dioxide is passed for a long time (say 24 hours) and the ends are sealed. The lower ends of both the tubes are immersed in mercury and the lower ends of the tubes are opened under mercury. A small pellet of mercury is drawn in both the tubes by alternately heating and cooling the tubes. These mercury pellets act as stoppers. Both the tubes are fixed in a *H*-shaded copper vessel having steel stoppers *S*, *S*.

The vessel contains water and the screws are turned so that the mercury pellets in the two tubes appear above the vessel. The capillary tubes of *A* and *B* are calibrated to read volume directly.

Since the pressures of air in *A* and CO_2 in *B* are the same, from the volume of air in *A*, pressure of CO_2 in *B* can be calculated.

The volume of CO_2 is read directly from the tube *B*.

The experiment is performed by maintaining the capillary tube of *A* at a fixed temperature and the capillary tube of *B* at any desired temperature. Different pressures are applied at a fixed temperature of CO_2 and the readings are taken until the volumes are too small. Pressure can be increased by screwing in the plungers *S*, *S*.

The experiment is repeated, maintaining CO_2 at different temperatures. Thus different sets of readings of pressure and volume for carbon dioxide at various temperatures are obtained. A graph is plotted between pressure and volume at various temperatures (Fig. 5·15).

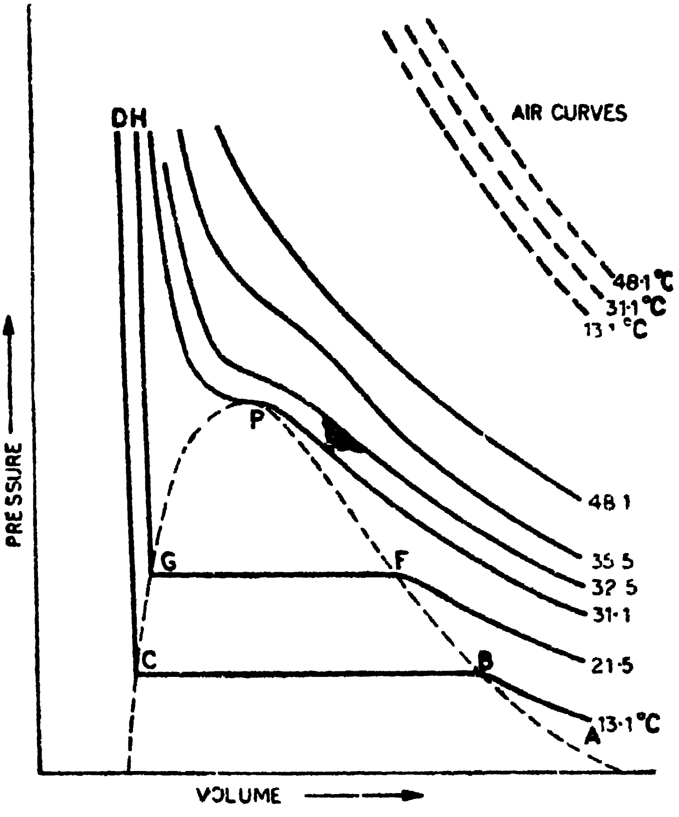


Fig. 5·15

The isothermals of CO_2 at various temperatures are shown in Fig. 5 15.

At 13·1°C, the portion *AB* represents the gaseous state of CO_2. Upto the point *B*, it obeys Boyle's law. From *B* to *C* it shows an enormous decrease in volume with slight increase in pressure. The portion *BC* represents the change of CO_2 from the gaseous to the liquid state. At *C* the whole of the gas has been liquefied. The portion *CD* represents the liquid state of CO_2 *i.e.*, there is no appreciable decrease in volume with increase in pressure.

At 21·5°C the curve is similar. The horizontal portion of the curve (FG) has decreased.

At 31·1°C the horizontal portion vanishes. It shows that the gas cannot be liquefied any more and its volume diminishes with increase in pressure.

The isothermals at 32·5°C and 35·5°C show the same behaviour and the portion of large compressibility decreases.

At 48·1°C the curve becomes smooth and it is similar to that of a permanent gas and it obeys Boyle's law.

Andrews found that the liquefaction of CO_2 occurred only below 31·1°C. This temperature is called the *critical temperature.*

Critical temperature of a gas is defined as that temperature below which the gas can be liquefied by the application of pressure alone. Above the critical temperature, the gas cannot be liquefied howsoever large the applied pressure may be.

In the graph, the pressure, volume and temperature corresponding to the point P are called the critical pressure (P_c), critical volume (V_c) and critical temperature (P_c).

Critical pressure is the pressure applied to the gas at its critical temperature so that it gets liquefied.

Critical volume is the particular volume of a gas at critical pressure and critical temperature.

Results

(*i*) There is no physical distinction between the liquid and the gaseous state of a substance. This is shown by the horizontal portions of the isothermals.

(*ii*) Below the critical temperature a gas can be liquefied under the application of pressure alone. The critical temperature for oxygen is −118 8°C ; for nitrogen −147·1°C ; and for hydrogen −240°C. Even these gases can be liquefied under the application of pressure if they are below the critical temperature. These gases have also been liquefied and they are no longer permanent gases.

(*iii*) The density of the vapour and the liquid became equal at the critical point. At the critical temperature the boundary line between the vapour and the liquid vanishes. Moreover, the compressibility of the vapour is infinite at the critical point.

5·33 Amagat's Experiment

Amagat performed a series of experiments with hydrogen (1878) and nitrogen (1893) to study their behaviour at high pressures. The apparatus consisted of a large metallic cylinder containing mercury having a screw S fitted to its one end. The apparatus was arranged at the base of a mine. A steel manometer tube of length about 300 metres was fixed along the shaft of the coal mine. The manometer tube was open at the top end. A calibrated inverted tube A

containing nitrogen (or hydrogen) was fitted to the cylinder containing mercury (Fig. 5·16). An oil bath surrounded the tube A and

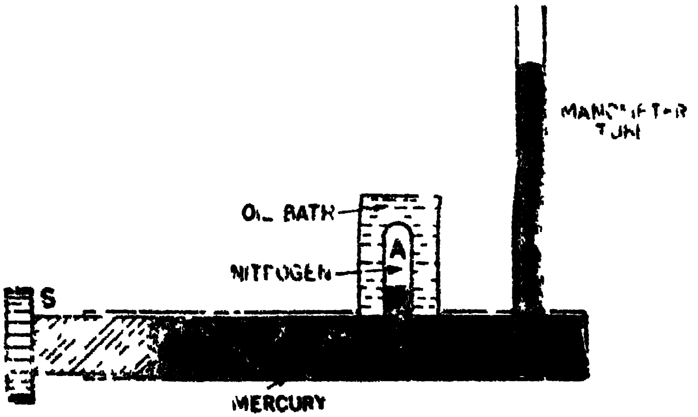


Fig. 5·16

the temperature of nitrogen could be kept fixed at any desired value. The tube A was calibrated to read the volume of the gas directly.

The difference in level of mercury columns in the tube A and the manometer tube measured the pressure on the gas. With this arrangement pressures up to 420 atmospheres could be applied.

Amagat plotted the isothermals between PV and P from the experimental data. He obtained the following results :

(1) For gases like air, oxygen, nitrogen, CO_2, ethylene etc., at low pressure, the product PV decreases with increase in P.

(2) With increase in pressure, the product PV attains a minimum value and then shows a steady increase with increase in P.

(3) In the case of hydrogen, the value of PV increases steadily with increase in P.

5·34 Holborn's Experiment

In 1915, Holborn and his co-workers performed a series of experiments to study the behaviour of gases at high pressures.

The apparatus consists of a glass bulb A connected to a manometer M, the globes B_1, B_2, B_3 ..., etc., and the pressure balance (Fig. 5·17).

The pressure balance consists of a fixed block E. A piston C fits into the hole in the block E. The piston C balances the pressure exerted by the gas through the oil in the cavity of the block. The piston C is kept at a fixed mark by adjusting the weight W. The total weight exerted on the oil is due to the weight of W, D, S, and C. Let the total weight be Mg and the area of cross-section of the piston C be a. The downward pressure due to the weight $= \frac{Mg}{a}$. This is also equal to the pressure of the gas in the bulb A.

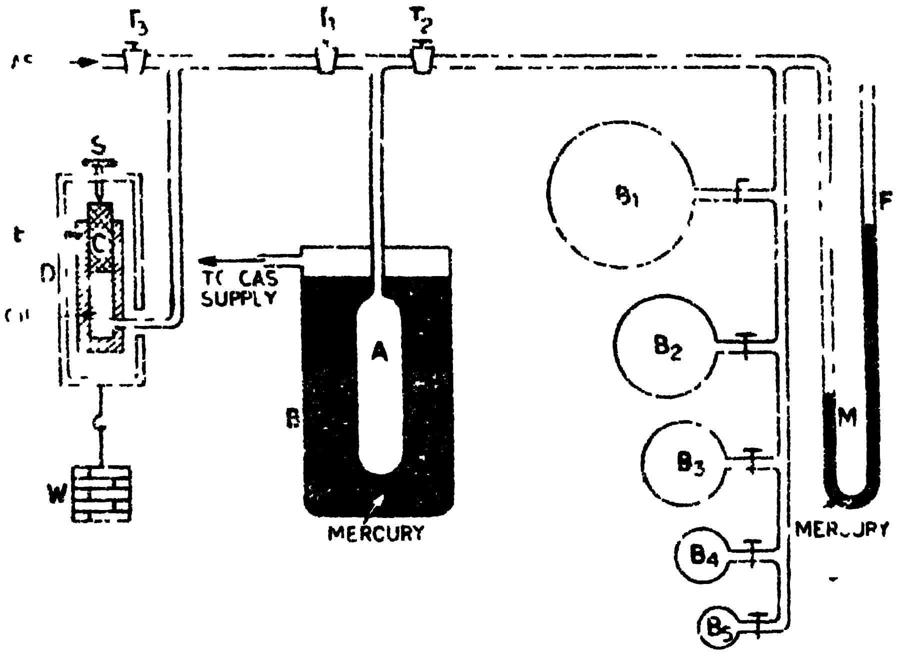


Fig. 5·17.

Initially the bulbs B_1, B_2 and B_3... etc. and A are evacuated. The stop-cock T_2 is closed. Gas at high pressure is admitted by opening the stop-cocks T_3 and T_1. The stop-cock T_3 is closed and the pressure of the gas in A is measured with the help of the pressure balance as explained above.

The stop-cock T_1 is closed and the stop-cock T_2 is opened. The stop-cocks of the bulbs B_1, B_2, etc. are opened one after the other till the pressure of the gas in A and the bulb is approximately equal to the atmospheric pressure. The volume of the bulbs, the connecting tubes and the bulb A is accurately known. The bulb A is enclosed in a bath containing the gas at high pressure to avoid the breakage of the bulb at high pressure.

Let the pressure of the gas as measured with the pressure balance be P_1, where $P_1 = \frac{Mg}{a}$. Let m_1 be the mass of the gas enclosed in A and m be the gram molecular weight of the gas. Then

$$PV_1 = \frac{m_1}{m} . RT$$

Here V_1 is the volume of the gas after expansion.

From this, the value of m_1 is calculated. Here P is the pressure of the gas after expansion and T is the temperature of the gas. If the volume of the gas admitted initially in the bulb $A = V_0$, then m_1 grams of the gas at a pressure P_1 occupies a volume V_0 at a temperature T.

Suppose in the second set of readings P_2 is the pressure of the gas and V_2 is the volume after expansion. If m_2 is the mass of the gas in A, then

$$PV_2 = \frac{m_2}{m}RT$$

From this equation m_2 is calculated.

If V_0 is the volume of the gas in A before expansion, then the volume of the gas for m_1 grams at a pressure P_2

$$= \frac{V_0 \times m_1}{m_2}$$

Thus the volume occupied by the same mass of the gas in a range of pressures and at different temperatures can be calculated.

5·35 Behaviour of Gases at High Pressure

The isothermals between PV and P for various gases have been drawn and the general nature of the curves is as shown in Fig. 5·18. The general nature of the curves is the same for all gases.

(1) At high temperature, the value of PV increases with increase in P.

(2) At lower temperatures, the value of PV decreases initially with increase in P. It becomes a minimum at a particular pressure and then increases with increase in pressure. The locus of these minima is shown by the dotted curve A.

(3) At temperatures below the critical temperature, there is a sudden decrease in the value of PV with increase in pressure. This corresponds to the change of state from gas to liquid. When the liquefaction is complete, PV gradually increases with increase in P. The shaded area represents the region of liquefaction.

Based on the experimental results of Andrews, Amagat and Holborn, K Onnes suggested an empirical relation

$$PV = A + BP + CP^2 + DP^3 \ldots\ldots \qquad \ldots(i)$$

Here A, B, C, D etc. are constants depending on the nature of the gas. These constants are called ***virial coefficients***. These constants change with temperature. The constant B has a special importance. Its value is negative at low temperatures and its value increases through zero to positive values at higher temperatures. The temperature at which the coefficient B is zero is called the **Boyle temperature**. At the Boyle temperature,

$$PV = A = \text{constant}$$

and
$$B = \frac{d\,[PV]}{dP} = 0$$

Below the Boyle temperature, the gases are highly compressible and this suggests the existence of inter-molecular attractions Beyond

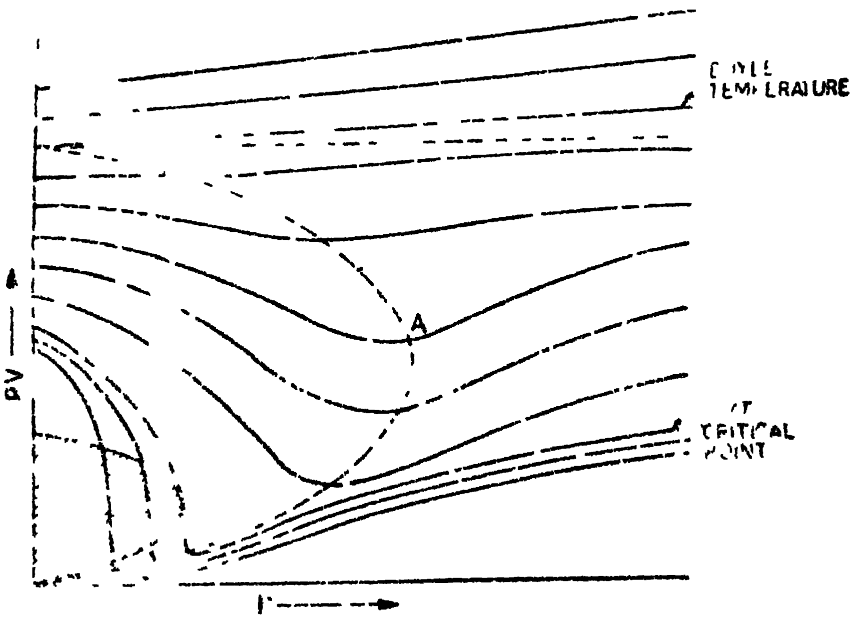


Fig. 5·15.

the Boyle temperature Boyle's law is obeyed and intermolecular attractions are less significant

5 36 Van der Waals Equation of State

While deriving the prefect gas equation $PV = RT$ on the basis of kinetic theory, it was assumed that (*i*) the size of the molecule of the gas is negligible and (*ii*) the forces of inter-molecular attraction are absent. But in actual practice, at high pressure, the size of the molecules of the gas becomes significant and cannot be neglected in comparison with the volume of the gas Also, at high pressure, the molecules come closer and the forces of intermolecular attraction are appreciable. Therefore, correction should be applied to the gas equation.

(*i*) Correction for Pressure. A molecule in the interior of a gas experiences forces of attraction in all directions and the resultant cohesive force is zero. A molecule near the walls of the container experiences a resultant force inwards (away from the wall). Due to this reason the observed pressure of the gas is less than the actual pressure. The correction for pressure p depends upon (*i*) the number of molecules striking unit area of the walls of the container per second and (*ii*) the number of molecules present in a given volume. Both these factors depend on the density of the gas.

$$\therefore \quad \text{Correction for pressure } p \propto \rho^2 \propto \frac{1}{V^2}$$

$$p = \frac{a}{V^2}$$

Here a is a constant and V is the volume of the gas

Hence correct pressure

$$= (P+p) = \left(P+\frac{a}{V^2}\right)$$

where P is the observed pressure.

(ii) Correction for Volume. The fact that the molecules have finite size shows that the actual space for the movement of the molecules is less than the volume of the vessel. The molecules have the sphere of influence around them and due to this factor, the correction for volume is b where b is approximately four times the actual volume of the molecules. Therefore the corrected volume of the gas $= (V-b)$.

Let the radius of one molecule be r.

The volume of the molecule

$$= x = \frac{4}{3}\pi r^3$$

The centre of any two molecules can approach each other only by a minimum distance of $2r$ *i.e.*, the diameter of each molecule. The volume of the sphere of influence of each molecule,

$$S = \frac{4}{3}\pi (2r)^3 = 8x$$

Consider a container of volume V. If the molecules are allowed to enter one by one,

The volume available for first molecule

$$= V$$

Volume available for second molecule

$$= V-S$$

Volume available for third molecule

$$= V-2S$$

... .

Volume available for nth molecule

$$= V-(n-1)\,S$$

Average space available for each molecule

$$= \frac{V+(V-S)+(V-2S)+\ldots\ldots V-(n-1)S\}}{n}$$

$$= V-\frac{S}{n}\{1+2+3\ldots\ldots(n-1)\}$$

$$= V-\frac{S}{n}\cdot\frac{(n-1)n}{2}$$

$$= V-\frac{nS}{2}+\frac{S}{2}$$

As the number of molecules is very large $\frac{S}{2}$ can be neglected.

$\therefore$ Average space available for each molecule

$$= V - \frac{nS}{2} \qquad \text{(But } S = 8x\text{)}$$

$$= V - \frac{n(8x)}{2}$$

$$= V - 4(nx)$$

$$= V - b$$

$\therefore$ $b = 4(nx) =$ four times the actual volume of the molecules

Thus the Van der Waals equation of state for a gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \text{...(i)}$$

where a and b are Van der Waals constants.

From the Van der Waals equation of state

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad \text{...(ii)}$$

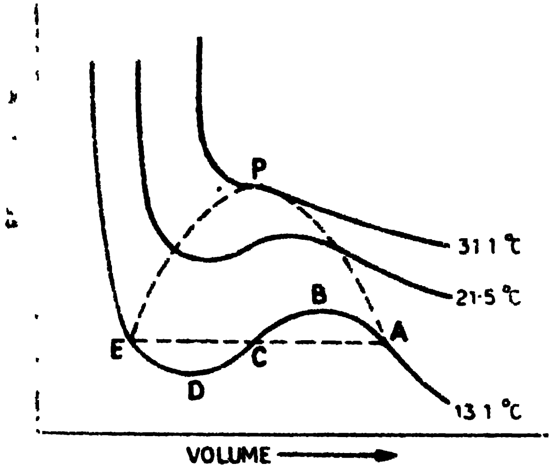


Fig. 5·19

Graphs between pressure and volume at various temperatures are drawn using equation (i). The graphs are as shown in Fig. 5·19. In the graph, the horizontal portion is absent. But in its place, the curve *ABCDE* is obtained. This does not agree with the experimental isothermals for CO_2 as obtained by Andrews. However, the portion *AB* has been explained as due to supercooling of the vapours and the portion *ED* due to super-heating of the liquid. But the portion *BCD* cannot be explained because it shows decrease in volume with decrease in pressure. It is not possible in actual practice. The states AB and ED, though unstable, can be realized in practice by careful experimentation. At higher temperatures, the theoretical and experimental isothermals are similar.

Until now as many as 56 different equations of state have been suggested. But no single equation satisfies all the observed facts.

Dicterice (1901) has suggested an equation

$$P(V-b) = RT\, e^{-\frac{a}{RTV}}$$

Berthelot has suggested an equation

$$\left(P+\frac{a}{V^2T}\right)(V-b) = RT$$

5·37 Critical Constants

The critical temperature and the corresponding values of pressure and volume at the critical point are called the critical constants. At the critical point, the rate of change of pressure with volume $\left(\frac{dP}{dV}\right)$ is zero. This point is calledthe point of inflexion.

According to Van der Waals equation

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT \qquad \text{...}(i)$$

$$P = \left(\frac{RT}{V-b}\right) - \frac{a}{V^2} \qquad \text{...}(ii)$$

Differentiating P with respect to V

$$\frac{dP}{dV} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} \qquad \text{...}(iii)$$

At the critical point $\frac{dP}{dV} = 0$

$$T = T_c$$

$$V = V_c$$

$$\therefore \quad \frac{-RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0$$

or

$$\frac{2a}{V_c^3} = \frac{RT_c}{(V_c-b)^2} \qquad \text{...}(iv)$$

Differentiating equation (*iii*)

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4}$$

At the critical point $\frac{d^2P}{dV^2} = 0$,

$$T = T_c,$$

$$V = V_c$$

$$\therefore \qquad \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0$$

$$\frac{6a}{V_c^4} = \frac{2RT_c}{(V_c-b)^3} \qquad \text{...(v)}$$

Dividing (*iv*) by (*v*)

$$\frac{V_c}{3} = \frac{V_c-b}{2}$$

or

$$2V_c = 3V_c - 3b$$

$$V_c = 3b \qquad \text{...(vi)}$$

Substituting the value of

$$V_c = 3b \text{ in equation } (iv)$$

$$\frac{2a}{27b^3} = \frac{RT_c}{4b^2}$$

or

$$T_c = \frac{8a}{27Rb} \qquad \text{...(vii)}$$

Substituting these values of V_c and T_c in equation (*ii*)

$$P_c = \frac{R \times 8a}{27Rb(2b)} - \frac{a}{9b^2}$$

$$P_c = \frac{a}{27b^2} \qquad \text{...(viii)}$$

5·38 Corresponding states

Two gases are said to be in corresponding states if the ratios of their actual pressure, volume and temperature and critical pressure, critical volume and critical temperature have the same value. It means

$$\frac{P_1}{P_{c1}} = \frac{P_2}{P_{c2}}$$

$$\frac{V_1}{V_{c1}} = \frac{V_2}{V_{c2}}$$

and

$$\frac{T_1}{T_{c1}} = \frac{T_2}{T_{c2}}$$

TABLE

Critical Temperature and Pressure of Common Gases

Substance	*Critical Temperature °C*	*Critical Pressure (atmospheres)*
Helium	−268°C	2.2[illegible]
Hydrogen	−240°C	12.8[illegible]
Nitrogen	−14[illegible]	33.[illegible]
Air	[illegible]	39.[illegible]
[illegible]	−1[illegible]	1[illegible]
[illegible]	31[illegible]	[illegible]
[illegible]		73.[illegible]
Ammonia	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

5.39 Coefficient of Van der Waals Constants

$$[illegible] \qquad \ldots(i)$$

$$P_c = \frac{a}{27b^2} \qquad \ldots(ii)$$

$$T_c = \frac{8a}{27Rb} \qquad \ldots(iii)$$

From equations (iii) and (ii)

$$\frac{T_c^2}{P_c} = \frac{64a^2}{(27)^2R^2b^2} \times \frac{27b^2}{a}$$

$$= \frac{64a}{27R^2}$$

$$\therefore \qquad a = \frac{27}{64}\frac{R^2T_c^2}{P_c} \qquad \ldots(iv)$$

Dividing (iii) by (ii)

$$\frac{T_c}{P_c} = \frac{8a}{27Rb} \times \frac{27b^2}{a}$$

$$= \frac{8b}{R}$$

$$b = \frac{RT_c}{8P_c} \qquad \ldots(v)$$

Also

$$\frac{RT_c}{P_cV_c} = \frac{R\,(8a)\,.\,27b^2}{27\,Rb\,a\,(3b)}$$

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} \qquad \ldots(91)$$

The quantity $\frac{RT_c}{P_cV_c}$ is called the *critical coefficient* of a gas. Its calculated value $= \frac{8}{3}$ and it is the same for all gases.

The experimental values of the critical coefficient for different gases is given below.

TABLE

Experimental Values of Critical Coefficient $\frac{RT_c}{P_cV_c}$

Substance	T_c in K	P_c in atm.	Specific volume in cm³/g	$\frac{RT_c}{P_cV_c}$
Helium	5.3	2.26	15.4	3.13
Hydrogen	33.1	12.8	32.2	3.28
Nitrogen	126.0	33.5	3.21	3.42
Oxygen	154.2	49.7	2.32	3.42
Carbon dioxide	304	72.8	2.17	3.48
Water	647	218	3.181	4.30

Note Here V_c = molecular wt × specific volume

The experimental value of the critical coefficient of all gases is greater than the theoretical value of 2.67

Example 5.24. *Calculate the Van der Waals constants for dry air, given that*

$T_c = 132$ K, $P_c = 37{\cdot}2$ atmospheres,

R per mole = 82·07 cm³ atmos K⁻¹. *(Delhi 1975)*

Here $P_c = 37{\cdot}2$ atmospheres

$T_c = 132$ K

$R = 82{\cdot}07$ cm³ atmos K⁻¹

(i) $$a = \frac{27}{64}\,\frac{R^2T_c^2}{P_c}$$

$$a = \left(\frac{27}{64}\right)\frac{(82{\cdot}07)^2(132)^2}{37{\cdot}2}$$

or $$a = \mathbf{13{\cdot}31 \times 10^6 \text{ atmos cm}^6}$$

(ii) $$b = \frac{RT_c}{8P_c}$$

$$b = \frac{82.07 \times 132}{8 \times 37.2}$$

or $$b = \mathbf{36.41\ cm^3}$$

5·40 Reduced Equation of State

Taking the pressure volume and temperature of a gas in terms of reduced pressure, volume and temperature,

$$\frac{P}{P_c} = \alpha, \quad \frac{V}{V_c} = \beta, \quad \frac{T}{T_c} = \gamma$$

$$P = \alpha P_c, \; V = \beta V_c, \; T = \gamma T_c$$

According to Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad \ldots(i)$$

or $$\left(\alpha P_c + \frac{a}{\beta^2 V_c^2}\right)(\beta V_c - b) = R\gamma T_c$$

But $$P_c = \frac{a}{27 b^2}$$

$$V_c = 3b$$

and $$T_c = \frac{8a}{27 Rb}$$

$$\therefore \left[\frac{\alpha a}{27 b^2} + \frac{a}{\beta^2 9b^2}\right][\beta . 3b - b] = \frac{R\gamma\, 8a}{27 Rb}$$

$$\left[\alpha + \frac{3}{\beta^2}\right][3\beta - 1] = 8\gamma \qquad \ldots(ii)$$

This is the reduced equation of state for a gas. If two gases have the same values of α, β and γ they are said to be in corresponding states.

5·41 Properties of Matter Near Critical Point

Based on the experiments of Andrews, Amagat and others, the state of matter near the critical point can be summarised as follows :—

(1) The densities of the vapour and the liquid gradually approach each other and their densities are equal at the critical point.

(2) At the critical point or just near the critical point, the line of demarcation between the liquid and the vapour disappears. Consequently, there must exist mutual diffusion between the two phases and the surface tension must be zero. This also means that the forces of inter molecular attraction in the liquid and vapour states must be equal at the critical point.

(3) The whole mass of the substance exhibits a flickering experience which indicates that there may be variations of density inside the mass. This has been experimentally verified.

(4) The compressibility of the vapour becomes infinite at the critical temperature.

The experiments performed by Callendar and others have shown that the densities of the liquid and vapour are not equal at the critical temperature. The densities are equal at a temperature slightly higher than the critical temperature. The critical temperature of water is 374°C. It was found that the densities are equal at 380°C. At 374°C the latent heat of water was found to be 72·4 calories per gram. At 380°C the latent heat of water is zero.

To conclude, the critical point for any substance is not a particular temperature but it is a narrow region (critical region). **The critical point is that point at which the properties of the two phases become identical.**

5 42 Experimental Determination of Critical Constants

(1) The critical constants can be determined by plotting the isothermals between *P* and *V* at different temperatures of the gas. The critical point is found on the graph, where the horizontal portion of the curve (change from gaseous to the liquid state) just vanishes. The pressure, volume and temperature corresponding to the critical point give the *critical constants* of the gas.

(2) With the help of Cagniard de la Tour's apparatus, the temperatures at which the liquid meniscus disappears and reappears are carefully noted. The mean of these two temperatures gives the critical temperature of the gas. The bulb is surrounded by a bath whose temperature is controlled by a sensitive thermostat and the temperature is varied by small amounts (say 0·1°C). The pressure is read with the help of a manometer. The pressure corresponding

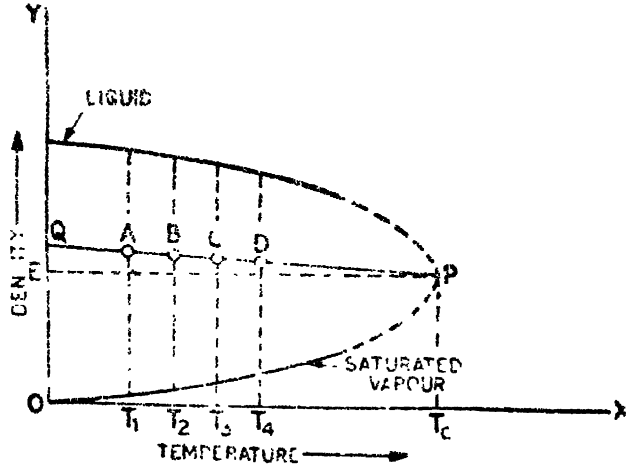


Fig. 5·20

to the critical temperature gives the critical pressure. However, the measurement of critical volume offers a practical difficulty because even if the temperature is slightly below the critical temperature, the change in volume is enormous even for a small change in pressure.

(3) Cailetet and Mathias have suggested a method for the determination of critical volume. Density of the liquid is determined accurately at different temperatures. The density of the saturated vapour is also determined accurately for the same temperature range. A graph is plotted between density and temperature (Fig. 5·20).

The density of the liquid decreases with rise in temperature and that of the saturated vapour increases with rise in temperature. On the graph the points A, B, C and D represent the mean density of liquid and the vapour at temperatures T_1, T_2, T_3, T_4 etc. respectively.

The points lie on a straight line The line is produced and the curves are extrapolated to meet the line at the point P. The density corresponding to the point P is obtained from the graph. Let this density be ρ.

The specific volume *i.e.* volume per unit mass

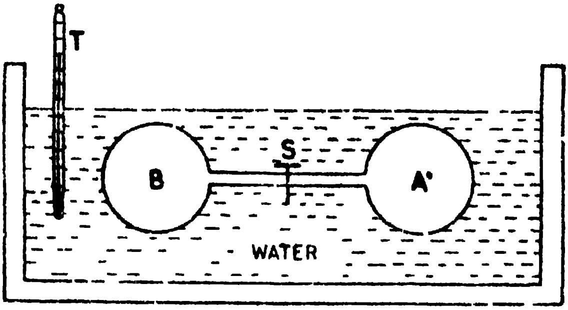
$$V_c = \frac{1}{\rho}$$

This represents the critical volume. The temperature corresponding to the point P gives the critical temperature.

5·43 Inter-molecular Attraction

Joule's Experiment. Joule performed an experiment to study the inter-molecular attraction between the molecules of a gas. He designed an apparatus to measure the change in energy of a gas when its pressure and volume are changed

A and B are two flasks connected by a tube and fitted with a stop cock S. A was filled with the gas at high pressure and B was perfectly evacuated (Fig. 5·21). The bulbs were surrounded by a water bath and its temperature was noted with a sensitive thermometer. The stop-cock was opened and the gas rushed from A to B If work was done during expansion, cooling was expected.



Fig· 5·21

But in this experiment no cooling was observed. This was puzzling as the work had been done by the gas in overcoming the forces of inter-molecular attractions. Joule was able to explain the drawback in his experiment by assuming that the gas has expanded into vacuum and so no cooling was observed.

In this experiment only the pressure and volume of the gas changed and as the bath did not show any change in temperature, it is evident that the temperature of the gas remained constant.

According to Joule, this experiment also shows that the internal energy of a gas is a function of temperature only, irrespective of the changes in pressure and volume

The porous plug experiment designad by Joule and Kelvin, however, showed cooling due to the work done by a gas in overcoming the inter-molecular attraction when it was passed from the high pressure to the low pressure side.

5·44 Porous Plug Experiment

The apparatus consists of a porous plug having two perforated brass discs D, D. The space between them is packed with cotton

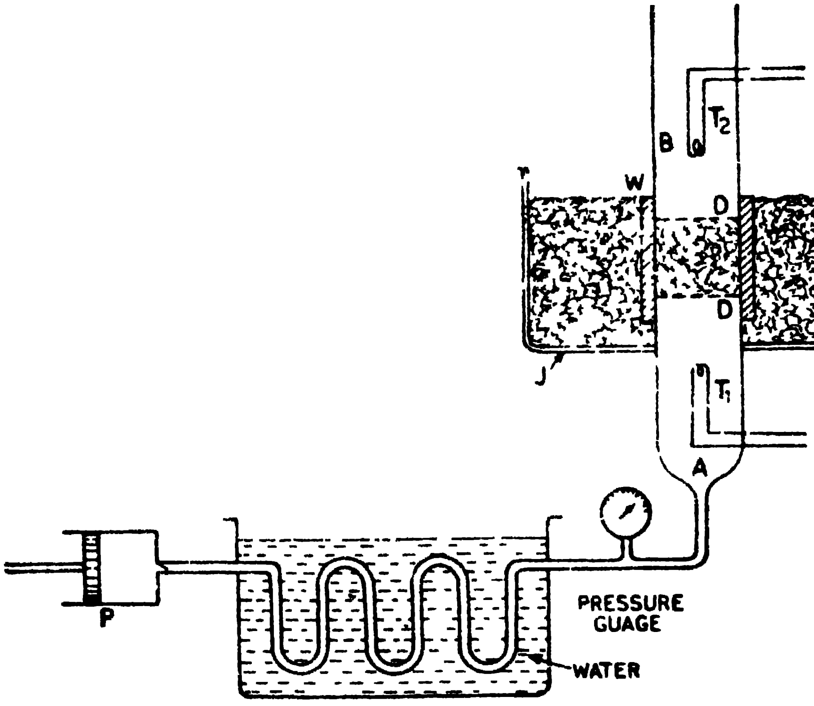


Fig. 5·22.

wool or silk fibres. The porous plug is fitted in a cylindrical box wood tube which is surrounded by a vessel containing cotton wool (Fig. 5·22). This is done to avoid loss or gain of heat from the surroundings. T_1 and T_2 are two sensitive platinum resistance thermometers and they measure the temperatures of he incoming and the outgoing gas. The gas is compressed to a high pressure with the help of the piston P and it is passed through a spiral tube immersed in a water bath maintained at a constant temperature. If there is any heating of the gas due to compression, this heat is taken by the circulating water in the water bath.

The compressed gas is passed through the porous plug. The gas gets throttled (wire drawn) due to cotton wool. Work is done by the gas in overcoming inter-molecular attraction. The temperature of the outgoing gas is measured with the help of a platinum resistance thermometer T_2. The pressure of the incoming gas is measured with the help of a pressure gauge and the pressure of the outgoing gas is equal to the atmospheric pressure.

The behaviour of a large number of gases was studied at various inlet temperatures of the gas and the results obtained are as follows :

(*i*) At sufficiently low temperatures all gases show a cooling effect.

(*ii*) At ordinary temperatures all gases except hydrogen and helium show cooling effect. Hydrogen shows heating instead of cooling at room temperature

(*iii*) The fall in temperature is directly proportional to the difference in pressure on the two sides of the porous plug.

(*iv*) The fall in temperature per atmosphere difference of pressure decreases as the initial temperature of the gas is raised. It becomes zero at a particular temperature and at temperature higher than this temperature, instead of cooling, heating is observed. This particular temperature at which the Joule Thomson effect changes sign is called the temperature of inversion.

In the case of hydrogen heating was observed at room temperature because it was at a temperature far higher than its temperature of inversion. The temperature of inversion for hydrogen is −80°C and for helium it is —258°C. If helium is passed through the porous plug at a temperature lower than —25 C it will also show cooling effect. It means any gas below the temperature of inversion shows a cooling effect when it is passed through the porous plug or a throttle valve.

5·45 Theory of Porous Plug Experiment

The simple arrangement of the porous plug experiment is shown in Fig. 5.21. The gas is allowed to pass through the porous plug from the high pressure side to the low pressure side. The velocity of the gas as it emerges from the porous plug is very high and there is increase in the kinetic energy of the molecules. Consider one gram molecule of a gas to the left and to the right of the porous plug. Let P_1, V_1 and P_2, V_2 represent the pressure and volume on the two sides of the porous plug. When the piston A is moved through a certain distance dx, the piston B also moves through the same distance dx. The work done *on the* gas by the piston $A = P_1 A_1 dx = P_1 V_1$. The work done by the gas on the piston B is $P_2 A_2 dx = P_2 V_2$. Thus, the net external work done by the gas is $P_2 V_2 - P_1 V_1$.

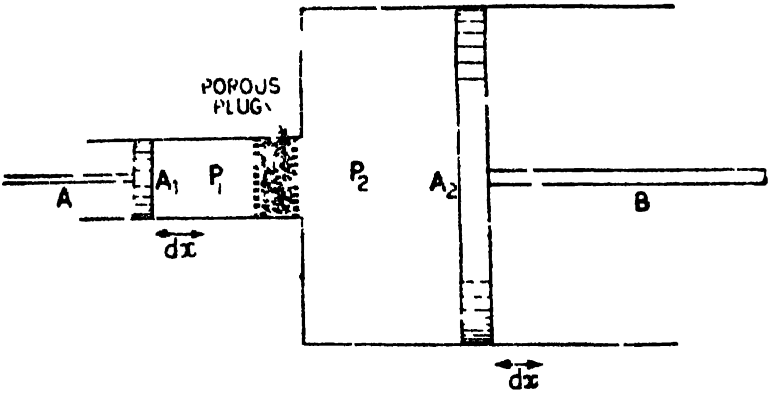


Fig. 5 23

If w is the work done by the gas in separating the molecules against their inter-molecular attractions, the total amount of work done by the gas is

$$(P_2 V_2 - P_1 V_1) + w$$

No heat is gained or lost to the surroundings. There are three possible cases :

(*i*) Below the Boyle temperature,

$$P_1 V_1 < P_2 V_2$$

and $P_2 V_2 - P_1 V_1$ is $+ve$. w must be either positive or zero. Thus a net positive work is done *by the gas* and there must be cooling when the gas passes through the porous plug

(*ii*) At the Boyle temperature if P_1 is not very high

$$P_1 V_1 = P_2 V_2$$

and $$P_2 V_2 - P_1 V_1 = 0$$

The total work done by the gas in this case is w. Therefore cooling effect at this temperature is only due to the work done by the gas in overcoming inter-molecular attractions.

(*iii*) Above the Boyle temperature

$$P_1 V_1 > P_2 V_2$$

or $$P_2 V_2 - P_1 V_1 \text{ is } -ve$$

Thus the observed effect will depend upon whether $(P_1 V_1 - P_2 V_2)$ is greater or less than w.

If $w > (P_1 V_1 - P_2 V_2)$, cooling will be observed.

If $w < (P_1 V_1 - P_2 V_2)$, heating will be observed.

This is the cooling or heating of a gas due to free expansion through a porous plug from a high pressure to a low pressure side will depend on (*i*) the deviation from Boyle's law and (*ii*) work done in overcoming inter-molecular attractions.

5·46. Joule-Kelvin Effect—Temperature of Inversion

Assuming that the Van der Waals equation is obeyed, the attractive forces between the molecules are equivalent to an internal pressure $\frac{a}{V^2}$.

When the gas expands from V_1 to V_2, the work done in overcoming inter molecular attractions

$$w = \int_{V_1}^{V_2} p.\,dV$$

But
$$p = \frac{a}{V^2}$$

∴
$$w = \int_{V_1}^{V_2} \frac{a}{V^2}\,dV$$
$$= -\frac{a}{V_2} + \frac{a}{V_1}$$

If V_1 and V_2 represent the gram molecular volumes on the high and the low pressure sides respectively, the external work done by the gas is

$$(P_2V_2 - P_1V_1)$$

Hence the total work done by the gas

$$W = (P_2V_2 - P_1V_1) + w$$
$$= (P_2V_2 - P_1V_1) - \frac{a}{V_2} + \frac{a}{V_1}$$

Van der Waals equation of state for a gas is

$$\left(P + \frac{a}{V^2}\right)\left(V - b\right) = RT$$

or
$$PV + \frac{a}{V} - bP - \frac{ab}{V^2} = RT$$

or
$$PV = RT + bP - \frac{a}{V}$$

$$\left[\frac{ab}{V^2} \text{ is negligible}\right]$$

$$W = \left[RT + bP_2 - \frac{a}{V_2}\right] - \left[RT + bP_1 - \frac{a}{V_1}\right] - \frac{a}{V_2} + \frac{a}{V_1}$$
$$= b\left[P_2 - P_1\right] + 2a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

But
$$V_1 = \frac{RT}{P_1} \text{ and } V_2 = \frac{RT}{P_2}$$

$$\therefore \qquad W = b\left[P_2 - P_1\right] + 2a\left[\frac{P_1}{RT} - \frac{P_2}{RT}\right]$$

or
$$W = -b\left[P_1 - P_2\right] + \frac{2a}{RT}\left[P_1 - P_2\right]$$

or
$$W = \left(P_1 - P_2\right)\left(\frac{2a}{RT} - b\right) \qquad \ldots(i)$$

Suppose the fall in temperature is δT

$$W = JH$$
$$= J\left[MC_P\,\delta T\right]$$

where M is the gram-molecular weight of the gas

$$\therefore \qquad JMC_P\,\delta T = \left(P_1 - P_2\right)\left(\frac{2a}{RT} - b\right)$$

or
$$\delta T = \left[\frac{P_1 - P_2}{JMC_P}\right] \times \left(\frac{2a}{RT} - b\right) \qquad \ldots(ii)$$

(i) Since $P_1 - P_2$ is +ve

δT will be +ve if $\left(\frac{2a}{RT} - b\right)$ is +ve

i.e.
$$\frac{2a}{RT} > b, \quad \text{or} \quad T < \frac{2a}{Rb} \qquad \ldots(iii)$$

Therefore cooling will take place if the temperature of the gas is less than $\frac{2a}{Rb}$

(ii) For δT to be zero, from equation (ii),

$$\frac{2a}{RT} - b = 0$$

or
$$T = \frac{2a}{Rb}$$

This temperature is called the temperature of inversion and is represented by T_i

$$T_i = \frac{2a}{Rb} \qquad \ldots(iv)$$

(iii) δT will be negative, if

$$\left(\frac{2a}{RT} - b\right) \text{ is } -\text{ve}$$

i.e.,
$$b > \frac{2a}{RT}$$

or
$$T > \frac{2a}{Rb}$$
$$T > T_i$$

Therefore heating will take place if the temperature of the gas is more than the temperature of inversion.

Results

(i) If the gas is at the temperature of inversion, then no cooling or heating is observed when it is passed through the porous plug.

(ii) If the gas is at a temperature lower than the temperature of inversion, cooling will take place when it is passed through the porous plug. This is called *regenerative cooling* or *Joule-Kelvin cooling*. This principle has been used in the liquefaction of the so-called permanent gases like nitrogen, oxygen, hydrogen and helium.

(iii) If the gas is at a temperature higher than the temperature of inversion, instead of cooling, heating is observed when the gas is passed through the porous plug.

5.47 Relation between Boyle Temperature, Temperature of Inversion and Critical Temperature

Temperature of inversion,

$$T_i = \frac{2a}{Rb} \qquad \ldots(i)$$

Boyle temperature

$$T_B = \frac{a}{Rb} \qquad \ldots(ii)$$

Critical temperature,

$$T_c = \frac{8a}{27\,Rb} \qquad \ldots(iii)$$

From (*i*) and (*ii*)

$$T_i = 2T_B \qquad \ldots(iv)$$

From (*i*) and (*iii*)

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \cdot \frac{27\,Rb}{8a}$$

$$= \frac{27}{4} = 6{\cdot}75$$

The experimental value of $\frac{T_i}{T_c}$ for actual gases is just less than 6.

It means that the temperature of inversion is very much higher than the critical temperature. For hydrogen $T_i = 190$ K and $T_c = 33$ K. As $T_i \gg T_c$, the methods employing regenerative cooling (Joule-Kelvin cooling) are preferred to those employing the initial cooling of the gas below the critical temperature.

Exercises V

1. Describe Andrews' experiments on carbon dioxide. Discuss the results obtained by him. Show that the liquid and the gaseous states are two distant stages of a continuous phenomenon.

2. Derive on the basis of kinetic theory of gases the laws for an ideal gas. *(Agra 1962)*

3. Give the theory of the porous plug experiment. (*Agra 1961*)

4. What are the critical constants of a gas? State and explain Van der Waals equation. Calculate the critical constants of gas in terms of the constants of this equation. (*Agra 1961*)

5. State the law of equipartition of energy. Prove the law for a perfect gas, whose molecules have *n* degrees of freedom. Show that for a mono-atomic gas $\gamma = 1{\cdot}66$ and for a diatomic gas $\gamma = 1{\cdot}40$. (*Agra 1963 ; Gorakhpur 1967*)

6. What is Joule-Thomson effect? Obtain an expression for the cooling produced in a Van der Waals gas. Hence explain why hydrogen and helium show heating effect at ordinary temperatures. [*Delhi (Hons.) 1971, Delhi 1972 ; Agra 1963 ; Lucknow 1964*]

7. Explain what you mean by degrees of freedom. State the law of equipartition of energy. Prove that for a perfect gas whose molecules have *n* degrees of freedom

$$\frac{C_P}{C_V} = 1 + \frac{2}{n}$$

Hence show that for a mono-atomic gas $\gamma = 1{\cdot}67$, for a diatomic gas $\gamma = 1{\cdot}4$ and for triatomic gas $\gamma = 1{\cdot}33$ (*Agra 1965*)

8. Derive Van der Waals equation. Deduce expressions for the critical constants in terms of *a* and *b*. (*Agra 1965 ; Delhi 1969 ; Delhi (Sub) 1966*)

9. Deduce from the kinetic theory of gases, an expression for the pressure of a gas. Also prove that

$$PV = RT$$

(*Delhi 1971 ; Agra 1966*)

10. Explain the corrections introduced by Van der Waals in the gas equation. Show that for a gas obeying Van der Waals equation

$$\frac{RT_c}{P_cV_c} = \frac{8}{3}$$

(*Gorakhpur 1967*)

11. Discuss briefly the considerations which led Van der Waals to modify the gas equation. What are the critical constants of a gas? Calculate the values of these constants in terms of the constants of the Van der Waals equation. (*Calcutta 1965 ; Delhi 1971, 73*)

12. Show that the pressure exerted by a perfect gas is $\frac{2}{3}$ of the kinetic energy of the gas molecules in a unit volume. (*Calcutta 1966*)

13. Derive and discuss the Van der Waals equation of state of a gas. Mention its defects. (*Rajasthan 1966*)

14. Define mechanical equivalent of heat and give its units in the C.G.S. system. Describe fully Searle's friction-cone method of determining the value of *J*. Discuss the necessary formula [illegible] [illegible]

15. Deduce Van dar Waals equation of state. How far does it conform to Andrews' experimental results on carbon dioxide ? What is the importance of Andrews' experiments in the problem of liquefaction of gases ? (*Panjab 1964*)

16. Describe the porous plug experiment. What conclusions have been drawn from it ? (*Delhi 1961*)

17. Describe Joule-Thomson effect and give its theory. (*Delhi 1967*)

18. Derive Maxwell's distribution law of velocities for gas molecules and discuss its experimental verification. (*Delhi 1966*)

19. What is meant by Joule-Kelvin effect ? How is it experimentally established ? How will you interpret the effect ? (*Panjab 1966*)

20. Describe Callendar and Barnes' continuous flow method for finding *J*.

21. Describe Jaegar and Steinwehr's method for finding the value of *J*.

22. Describe Holborn's experiments to study the behaviour of gases at high pressure.

23. Describe experiments to find the value of the critical constants of a gas.

24. Derive the relations between the Boyle temperature, temperature of inversion and critical temperature.

25. Derive an expression for the pressure exerted by gas on the basis of kinetic theory. (*Delhi 1969, 72, 73, 76*)

26 Describe the porous plug experiment and derive an expression for the Joule-Thomson cooling of a gas. What is inversion temperature ? (*Delhi 1968, 69, 77*)

27. Derive an expression for the mean free path of a molecule of a gas and describe a method for its determination.

28. Obtain an expression for the pressure of a gas on the basis of the kinetic theory of gases. Show that, according to the law of equipartition of energy the ratio of the two specific heats of ozone is 1·33. (*Delhi 1971*)

29. Distinguish between a perfect gas and a real gas. Derive Van der Waals equation of state and use it to obtain the expressions for the critical constants in terms of the constants of the Van der Waals equation. [*Delhi B.Sc.* (*Hons.*) *1972*]

30. What is the kinetic model of a gas ? How is pressure of a gas explained on this model ? Deduce an expression for the pressure ? (*Delhi B. Sc.* (*Hons.*) *1973*)

31. Describe briefly the porous plug experiment. Deduce a theoretical expression for the Joule-Thomson cooling for 1 gram molecule of a gas obeying Van der Waals equation of state. Why

does hydrogen show a negative Joule-Thomson effect ?
(Berhampur, 1972, Delhi B.Sc. (Hons.) 1973)

32. Distinguish between an adiabatic process and Joule-Thomson effect. Prove that for a Van der Waals gas the Joule-Thomson coefficient is given by

$$\left(\frac{\delta T}{\delta P}\right)=\frac{1}{C_p}\left[\frac{2a}{RT}-b\right]$$

(Delhi, 1974, Delhi B.Sc. (Hons.) 1972)

33. What is Joule-Thomson effect ? Derive an expression for Joule-Thomson cooling. What is temperature of inversion ? Prove that it is equal to $2a/Rb$. *(Delhi 1973)*

34. Show from the kinetic theory of gases that the mean kinetic energy of translation of a molecule of a gas is $3/2\ kT$, where k is the Boltzmann's constant. *(Delhi 1971)*

35. How is the ideal gas equation modified when mutual attraction between molecules and the finite size of the molecules are taken into consideration ? Obtain relations between critical constants and the constants appearing in the Van der Walls equation
(Delhi 1971)

36 Derive the reduced equation of state for a gas starting from Van der Waals equation of state. Show that if the two gases have the same reduced pressure and volume, they also have the same reduced temperature ? *(Delhi 1973)*

37 Starting from elementary ideas set up Van der Waals' equation of state and show how the constants of the equation can be expressed in terms of the critical constants. What is the experimental bearing of this equation ? *(Delhi 1975, 1976)*

38. Assuming the various postulates underlying the kinetic theory of gases, show that the mean kinetic energy of translation of a molecule is $3/2\ kT$. *(Delhi 1974)*

39. Derive Van der Waals equation for gases and calculate the theoretical values of the critical constants.
[Delhi (Hons.) 1974, Delhi 1977]

40. Show that the pressure exerted by a perfect gas is 2/3 of the mean kinetic energy per unit volume.
[Madras 1974, Delhi (Hons.) 1975]

41. On the basis of kinetic theory of gases, derive expressions for the thermal conductivity and viscosity of the gas. Hence obtain the relation between the two. *(Bombay 1974)*

42. Explain the basic principles of the kinetic theory of gases and show that the pressure of an ideal gas is proportional to its density. *(Delhi 1976)*

43. Deduce Van der Waals equation of state and obtain expressions for critical constants in terms of the constants of the equation. *(Kanpur 1975, Delhi 1976)*

44. Describe Andrews' experiments on carbon dioxide. Discuss the results obtained. What is the importance of these results in the liquefaction of gases ? (*Delhi 1976*)

45. How do you interpret (*i*) pressure and (*ii*) temperature on the basis of the kinetic theory of gases. (*Delhi 1976*)

46. What is the meaning of mean free path of the molecules of a gas ? Show that it is equal to $\frac{1}{\eta\pi\sigma^2}$. (*Delhi 1977*)

47. Give a discussion of Maxwellian distribution of speed C amongst N molecules per cm^3 enclosed in a chamber at a temperature T. (*Agra 1975*)

48. Express Maxwell's law of distribution of speeds in terms of the kinetic energy of the molecules. Hence find the most probable and the average energy of the molecules. [*Delhi* (*Hons.*) *1977*]

49. Derive an expression for the viscosity of a gas on the basis of the kinetic theory and discuss its dependence on temperature and pressure. [*Delhi* (*Hons.*) *1976*]

50. Obtain an expression for the thermal conductivity of an ideal gas on the basis of kinetic theory. Discuss its dependence on pressure and temperature. [*Delhi* (*Hons*) *1977*]

51. What do you understand by degrees of freedom of a molecule in a thermal system ? State the law of equipartition of energy.

Apply this law to obtain specific heats, C_p and C_v of gases. Compare the values of γ, the ratio of C_p and C_v, so obtained with the experimental results in the case of monoatomic, diatomic and polyatomic gases. Discuss the discrepancies wherever they occur. [*Delhi, 1978*]

52. Describe the aim of the porous-plug experiment and its predictions. Outline the important results of this experiment.

53. Derive an expression for the change in the temperature of a gas undergoing Joule-Thomson expansion. Discuss the role of inversion temperature in it. [*Delhi, 1978*]

54. Define viscosity of a fluid. Obtain an expression for the viscosity of an ideal gas on the basis of kinetic theory. [*Delhi* (*Hons.*), *1978*]

55. Calculate the total random kinetic energy of 1 gram molecule of nitrogen at 300 K. [**Ans.** 3,735 joules]

56. Calculate the average kinetic energy of a hydrogen molecule at 27°C. [**Ans.** $6{\cdot}21\times10^{-14}$ ergs]

57. Calculate the total random kinetic energy of 2 grams of nitrogen at 27°C. [**Ans.** 266·8 joules]

58. Calculate the total random kinetic energy of 8 grams of helium at 200 K. [**Ans.** 4,980 joules]

59. Calculate the r.m.s. velocity of a mercury atom at 1,200 K. [**Ans.** $3{\cdot}86\times10^4$ cm/s)

60. With what speed would 1 gram molecule of hydrogen at 27°C be moving in order that the translational kinetic energy of *its centre of mass is equal to the total random kinetic energy of all* its molecules ? (Molecular weight of hydrogen = 2)

[**Ans.** $1{\cdot}93 \times 10^5$ cm/s]

61. Calculate the temperature at which the r.m.s. velocity of a helium molecule will be equal to the speed of the earth's first satellite *i.e.*, $v = 8$ km/s. [**Ans.** $10{\cdot}28 \times 10^3$ K]

62. Calculate the mean kinetic energy of a molecule of a gas at 1,000°C. Given,

$$R = 8{\cdot}31 \times 10^7 \text{ ergs/gram mol-K}$$
$$N = 6{\cdot}02 \times 10^{23}$$

(*Delhi 1969*) [**Ans.** $2{\cdot}07 \times 10^{-13}$ ergs]

63. If the density of nitrogen is 1·25 g/litre at N.T.P., calculate the R.M.S. velocity of its molecules.

[*Delhi 1972* ; *Delhi* (*Hons.*) *1973*] [**Ans.** $4{\cdot}95 \times 10^4$ cm/s]

64. At what temperature is the R.M.S. speed of oxygen molecules twice their R.M.S. speed at 27°C ?

(*Delhi 1973*) [**Ans.** 927°C]

65. Calculate the R.M.S. velocity of the molecules of hydrogen at 0°C. Molecular weight of hydrogen = 2·016 and

$$R = 8{\cdot}31 \times 10^7 \text{ ergs/gram mole °C}$$

(*Delhi 1971*) [**Ans.** $18{\cdot}4 \times 10^4$ cm/s]

66. Calculate the R.M.S. velocity of the hydrogen molecules at room temperature, given that one litre of the gas at room temperature and normal pressure weighs 0·086 g.

(*Delhi 1976*) [**Ans.** $1{\cdot}88 \times 10^5$ cm/s)]

67. Write short notes on :

(*i*) Mean free path [*Agra 1962* ; *Delhi* (*Sub.*) *1966*]
(*ii*) Joule-Thomson Effect (*Agra 1962* ; *Delhi 1974, 75*)
(*iii*) Continuity of state
(*iv*) Rowland's experiment for finding *J*
(*v*) Van der Waals equation of state
(*vi*) Pressure exerted by an ideal gas
(*vii*) Critical constants
(*viii*) Degrees of freedom
(*ix*) Atomicity of gases
(*x*) Maxwell's law of distribution of velocity. (*Delhi 1975*)
(*xi*) Andrews' experiments
(*xii*) Amagat's experiments
(*xiii*) Halborn's experiments
(*xiv*) Behaviour of gases at high pressure
(*xv*) Critical point
(*xvi*) Corresponding states
(*xvii*) Intermolecular attraction
(*xviii*) Temperature of inversion
(*xix*) Reduced equation of state for a gas [*Delhi* (*Hons.*) *1976*]
(*xx*) Porous plug experiment.

6

Thermodynamics

6·1 Thermodynamic System

A thermodynamic system is one which can be described in terms of the thermodynamic co-ordinates The co-ordinates of a thermodynamic system can be specified by any pair of quantities *viz.*, pressure (P), volume (V), temperature (T) and entropy (S). The thermodynamic systems in engineering are gas, vapour, steam, mixture of gasoline vapour and air, ammonia vapours and its liquid. In Physics, thermodynamics includes besides the above, systems like stretched wires, thermocouples, magnetic materials, electrical condenser, electrical cells, solids and surface films

Examples · 1 Stretched wire. In a stretched wire, to find the Young's modulus of a wire by stretching, the complete thermodynamic co-ordinates are

(*a*) the stretching force F
(*b*) the length of the stretching wire and
(*c*) the temperature of the wire

The pressure and volume are considered to be constant.

2. Surface Films. For liquid films, in the study of surface tension, the thermodynamic co-ordinates are

(*a*) the surface tension
(*b*) the area of the film and
(*c*) the temperature.

3. Reversible Cells. The thermodynamic coordinates to completely describe a reversible cell are

(*a*) the E M F of the cell
(*b*) the charge that flows and
(*c*) the temperature

6.2 Thermal equilibrium and Concept of Temperature [Zeroth Law of Thermodynamics]

A thermodynamic system is said to be in thermal equilibrium if any two of its independent thermodynamic co-ordinates X and Y remain constant as long as the external conditions remain unaltered. Consider a gas enclosed in a cylinder fitted with a piston. If the pressure and volume of the enclosed mass of gas are P and V at the temperature of the surroundings, these values of P and V will remain constant as long as the external conditions viz. temperature and pressure remain unaltered. The gas is said to be in thermal equilibrium with the surroundings.

The *zeroth law* of thermodynamics was formulated after the first and the second laws of thermodynamics have been enunciated. This law helps to define the term *temperature* of a system.

This law states that *if, of three systems, A, B and C, A and B are separately in thermal equilibrium with C, then A and B are also in thermal equilibrium with one another.*

Conversely the law can be stated as follows.

If three or more systems are in thermal contact, each to each, by means of diathermal walls and are all in thermal equilibrium together then any two systems taken separately are in thermal equilibrium with one another.

Consider three fluids A, B and C. Let P_A, V_A represent the pressure and volume of A, P_B, V_B the pressure and volume of B, and P_C, V_C are the pressure and volume of C.

If A and B are in thermal equilibrium, then

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B)$$

or

$$F_1[P_A, V_A, P_B, V_B] = 0 \quad \text{...}(i)$$

Expression (i) can be solved and

$$P_B = f_1[P_A, V_A, V_B] \quad \text{...}(ii)$$

If B and C are in thermal equilibrium

$$\phi_2(P_B, V_B) = \phi_3(P_C, V_C)$$

or

$$F_2[P_B, V_B, P_C, V_C] = 0$$

Also

$$P_B = f_2[V_B, P_C, V_C] \quad \text{...}(iii)$$

From equations (ii) and (iii) for A and C to be in thermal equilibrium separately,

$$f_1(P_A, V_A, V_B) = f_2[V_B, P_C, V_C] \quad \text{...}(iv)$$

If A and C are in thermal equilibrium with B separately, then according to the zeroth law, A and C are also in thermal equilibrium with one another.

$$\therefore \quad F_3[P_A, V_A, P_C, V_C] = 0. \quad \text{...}(v)$$

Equation (iv) contains a variable V_B, whereas equation (v) does not contain the variable V_B. It means

$$\phi_1(P_A, V_A) = \varphi_3(P_C, V_C) \quad \text{...}(vi)$$

In general,

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) \qquad ...(vii)$$

These three functions have the same numerical value though the parameters (P, V) of each are different. This numerical value is termed as *temperature* (T) of the body.

$$\therefore \qquad \phi(P, V) = T \qquad ...(viii)$$

This is called the equation of state of the fluid.

Therefore, the temperature of a system can be defined as the property that determines whether or not the body is in thermal equilibrium with the neighbouring systems. If a number of systems are in thermal equilibrium, this common property of the system can be represented by a single numerical value called the temperature. It means that if two systems are not in thermal equilibrium, they are at different temperatures.

Example. In a mercury in glass thermometer, the pressure above the mercury column is zero and volume of mercury measures the temperature. If a thermometer shows a constant reading in two systems A and B separately, it will show the same reading even when A and B are brought in contact.

6·3 Concept of Heat

Heat is defined as *energy in transit.* As it is not possible to speak of work in a body, it is also not possible to speak of heat in a body. Work is either done on a body or by a body. Similarly, heat can flow from a body or to a body. If a body is at a constant temperature, it has both mechanical and thermal energies due to the molecular agitations and it is not possible to separate them. So, in this case, we cannot talk of heat energy. It means, if the flow of heat stops, the word heat cannot be used. It is only used when there is transfer of energy between two or more systems.

Consider two systems A and B in thermal contact with one another and surrounded by adiabatic walls.

For the system A,

$$H = U_2 - U_1 + W \qquad ...(i)$$

where H is the heat energy transferred. U_1 is the initial internal energy, U_2 is the final internal energy and W is the work done.

Similarly for the system B,

$$H' = U_2' - U_1' + W' \qquad ...(ii)$$

Adding (i) and (ii)

$$\therefore \qquad H + H' = (U_2 - U_1) + W + (U_2' - U_1') + W'$$

$$H + H' = [(U_2 + U_2') - (U_1 + U_1')] + (W + W') \qquad ...(iii)$$

The total change in the internal energy of the composite system

$$= [(U_2 + U_2') - (U_1 + U_1')]$$

The work done by the composite system $= W+W'$

It means that the heat transferred by the composite system $= H+H'$. But the composite system is surrounded by adiabatic walls and the net heat transferred is zero.

$$\therefore \qquad H+H' = 0$$

$$H = -H' \qquad \ldots(iv)$$

Thus, for two systems A and B in thermal contact with each other, and the composite system surrounded by adiabatic walls, the heat gained by one system is equal to the heat lost by the other system.

6·4 Quasistatic Process

A system in thermodynamical equilibrium must satisfy the following requirements strictly :—

(*i*) **Mechanical Equilibrium** For a system to be in mechanical equilibrium, there should be no unbalanced forces acting on any part of the system or the system as a whole.

(*ii*) **Thermal Equilibrium**. For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surroundings.

(*iii*) **Chemical Equilibrium**. For a system to be in chemical equilibrium, there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other.

When a system is in thermodynamic equilibrium and the surroundings are kept unchanged, there will be no motion and also no work will be done. On the other hand, if the sum of the external forces is altered, resulting in a finite unbalanced force acting on the system, the condition for mechanical equilibrium will not be satisfied any longer. This results in the following :—

(*i*) Due to unbalanced forces within the system, turbulence, waves etc. may be set up. The system as a whole may possess an accelerated motion.

(*ii*) Due to turbulence, acceleration etc. the temperature distribution within the system may not be uniform. There may also exist a finite temperature difference between the system and the surroundings.

(*iii*) Due to the presence of unbalanced forces and difference in temperature, chemical reaction may take place or there may be movement of a chemical constituent.

From this discussion, it is clear that a finite unbalanced force may cause the system to pass through *non-equilibrium* states. If during a thermodynamic process, it is desired to describe every state of a system by thermodynamic coordinates referred to the system as a whole, the process should not be brought about by a finite unbalanced force.

A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process can be considered as equilibrium states.

In actual practice, many processes closely approach a quasistatic process and may be treated as such with no significant error. Consider the expansion of a gas in a closed cylinder fitted with a piston. Initially weights are on the piston and the pressure of the gas inside the cylinder is higher than the atmospheric pressure. If the weights are small and are taken off slowly one by one, the process can be considered quasistatic. If, however, all the weights are removed at once, expansion takes place suddenly and it will be a non-equilibrium process. The system will not be in equilibrium at any time during this process.

A quasistatic process is an ideal concept that is applicable to all thermodynamic systems including electric and magnetic systems. It should be noted that conditions for such a process can never be satisfied rigorously in practice.

6·5 Heat—A Path Function

Heat is a path function. When a system changes from a state 1 to state 2, the quantity of heat transferred will depend upon the intermediate stages through which the system passes *i.e.*, its path. Hence heat is an **inexact differential** and is written as δH.

On integrating, we get

$$\int_{1A}^{2A} \delta H = H_{1A}^{2A}$$

Here, ${}_1H_2$ represents the heat transferred during the given process between the states 1 and 2 along a particular path A.

6·6 Work—A Path Function

Suppose that a system is taken from an initial equilibrium state 1 to a final equilibrium state 2 by two different paths A and B (Fig. 6·1). The processes are quasistatic.

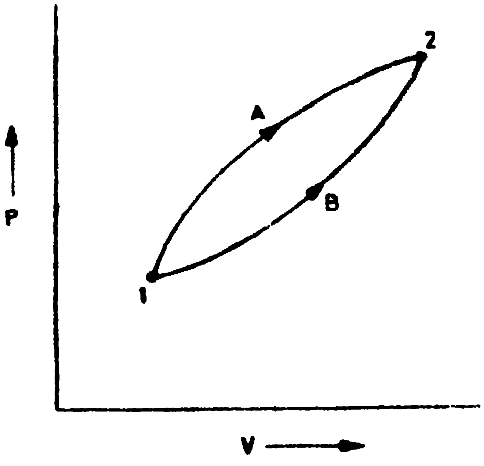


Fig. 6·1

The areas under these curves are different and hence the *quantities of work done are also different.*

For the path A,

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} P\,dV \qquad ...(i)$$

For the path B

$$W_B = \int_{1B}^{2B} \delta W = \int_{1B}^{2B} P\,dV \qquad ...(ii)$$

The values of W_A and W_B are not equal. Therefore work cannot be expressed as a difference between the values of some property of the system in the two states. *Therefore, it is not correct to represent*

$$W = \int_{W_1}^{W_2} \delta W = W_2 - W_1 \qquad (iii)$$

It may be pointed out that it is meaningless to say "work in a system or work of a system". Work cannot be interpreted similar to temperature or pressure of a system.

In terms of calculus δW is an inexact differential. It means that W is not a property of the system and $\int \delta W$ cannot be expressed as the difference between two quantities that depend entirely on the initial and the final states.

Hence, heat and work are **path functions** and they depend only on the process. They are not point functions such as pressure or temperature. Work done in taking the system from state 1 to state 2 will be different for different paths.

6 7 Comparison of Heat and Work

There are many similarities between heat and work. These are :—

1. Heat and work are both transient phenomena. Systems do not possess heat or work.

2. When a system undergoes a change, heat transfer or work done may occur.

3. Heat and work are boundary phenomena. They are observed at the boundary of the system.

4. Heat and work represent the energy crossing the boundary of the system.

5. Heat and work are path functions and hence they are inexact differentials. They are written as δH and δW.

6. (*a*) *Heat* is defined as the form of energy that is transferred across a boundary by virtue of difference of temperature or temperature gradient.

(*b*) Work is said to be done by a system if the sole effect on things external to the system could be the raising of a weight.

It is customary to represent, *work done by the system as +ve, work done on the system as —ve, heat flowing into the system as +ve, and heat flowing out of the system as —ve.*

6·8 First Law of Thermodynamics

Joule's law gives the relation between the work done and the heat produced. It is true when the whole of the work done is used in producing heat or *vice versa*. Here, $W = JH$ where J is the Joule's mechanical equivalent of heat. But in practice, when a certain quantity of heat is supplied to a system the whole of the heat energy may not be converted into work. Part of the heat may be used in doing external work and the rest of the heat might be used in increasing the internal energy of the molecules. Let the quantity of heat supplied to a system be δH, the amount of external work done be δW and the increase in internal energy of the molecules be dU. The term U represents the internal energy of a gas due to molecular agitation as well as due to the forces of inter-molecular attraction. Mathematically

$$\delta H = dU + \delta W \qquad \ldots(i)$$

Equation (*i*) represents the first law of thermodynamics. All the quantities are measured in heat units. The first law of thermodynamics states that the amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition. Therefore for a cyclic process $\oint dU = 0$

and
$$\oint \delta H = \oint \delta W \qquad \ldots(ii)$$

[Both are expressed in heat units]

This equation represents Joule's law.

For a system carried through a cyclic process, its initial and final internal energies are equal. From the first law of thermodynamics, for a system undergoing any number of complete cycles

$$U_2 - U_1 = 0$$

$$\oint \delta H = \oint \delta W$$

$$H = W \qquad \text{[Both are in heat units]}$$

6·9 First Law of Thermodynamics for a Change in State of a Closed System

For a closed system during a complete cycle, the first law of thermodynamics is written as

$$\oint \delta H = \oint \delta W$$

In practice, however, we are also concerned with a process rather than a cycle. Let the system undergo a cycle, changing its state from 1 to 2 along the path A and from 2 to 1 along the path B. This cyclic process is represented in the P—V diagram (Fig. 6·2).

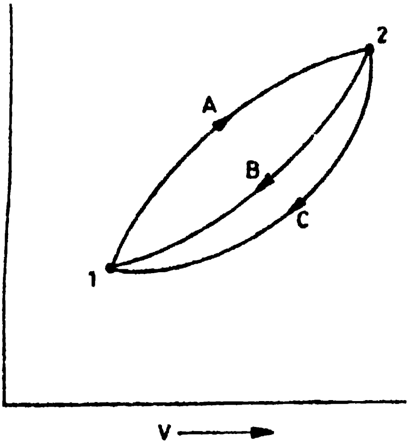


Fig. 6·2

According to the first law of thermodynamics

$$\oint \delta H = \oint \delta W$$

For the complete cyclic process

$$\int_{1A}^{2A} \delta H + \int_{2B}^{1B} \delta H = \int_{1A}^{2A} \delta W + \int_{2B}^{1B} \delta W \qquad \ldots(i)$$

Now, consider the second cycle in which the system changes from state 1 to state 2 along the path A and returns from state 2 to state 1 along the path C. For this cyclic process

$$\int_{1A}^{2A} \delta H + \int_{2C}^{1C} \delta H = \int_{1A}^{2A} \delta W + \int_{2C}^{1C} \delta W \qquad \ldots(ii)$$

Subtracting (*ii*) from (*i*)

$$\int_{2B}^{1B} \delta H - \int_{2C}^{1C} \delta H = \int_{2B}^{1B} \delta W - \int_{2C}^{1C} \delta W$$

or

$$\int_{2B}^{1B} (\delta H - \delta W) = \int_{2C}^{1C} (\delta H - \delta W) \qquad \ldots(iii)$$

Here B and C represent arbitrary processes between the states 1 and 2. Therefore, it can be concluded that the quantity $(\delta H - \delta W)$ is the same for all processes between the states 1 and 2. The quantity

$(\delta H-\delta W)$ depends only on the initial and the final states of the system and is independent of the path followed between the two states.

Let $$dE = (\delta H-\delta W)$$

From the above logic, it can be seen that

$$\int_1^2 dE = \text{constant and is independent of the path.}$$

This naturally suggests that E is a point function and dE is an exact differential.

The point function E is a property of the system.

Here dE is the derivative of E and it is an exact differential.

$$\therefore \quad \delta H-\delta W = dE \qquad \ldots(iv)$$

or $$\delta H = dE+\delta W \qquad \ldots(v)$$

Integrating equation (v), from the initial state 1 to the final state 2

$${}_1H_2 = (E_2-E_1)+{}_1W_2$$

[**Note.** ${}_1E_2$ cannot be written as (H_2-H_1), because it depends upon the path].

Similarly, ${}_1W_2$ cannot be written as (W_2-W_1), because it also depends upon the path.

Here ${}_1H_2$ represents the heat transferred,

${}_1W_2$ represents the work done,

E_2 represents the total energy of the system in state 2,

E_1 represents the total energy of the system in state 1.

At this point, it is worthwhile discussing what this E can possibly mean. With reference to the system, the energies crossing the boundaries are all taken care of in the form of H and W. For dimensional stability of Eq. (v), this E must be energy and this must belong to the system. Therefore,

E_2 represents the energy of the system in state 2

E_1 represents the energy of the system in state 1

This energy E acquires a value at any given equilibrium condition by virtue of its thermodynamic state. The working substance, for example a gas, has molecules moving in all random fashion. The molecules have energy associated by virtue of mutual attraction and this part is similar to the potential energy of a body in macroscopic terms. They also have velocities and hence kinetic energy. This energy E therefore can be visualised as comprising of molecular potential and kinetic energies in addition to macroscopic potential and kinetic energies. The first part, which owes its existence to the thermodynamic nature is often called the internal energy which is completely dependent on the thermodynamic state and the other two depend on mechanical or physical state of the system

$E = U + KE + PE +$ Others which depend upon chemical nature etc

For a closed system (non-chemical) the changes in all others except U are insignificant and

$$dE = dU$$

$\therefore$ From equation (i)

$$\delta H = dU + \delta W \qquad \ldots(ii)$$

Here all the quantities are in consistent units

Example 6 1. *When a system is taken from the state A to the state B, along the path ACB 80* joules *of heat flows into the system, and the system does 30* joules *of work (Fig 6 3).*

(*a*) *How much heat flows into the system along the path ADB, if the work done is 10* joules.

(*b*) *The system is returned from the state B to the state A along the curved path. The work done on the system is 20* joules. *Does the system absorb or liberate heat and how much ?*

(*c*) *If* $U_A = 0$, $U_D = 40$ joules, *find the heat absorbed in the process AD and DB*

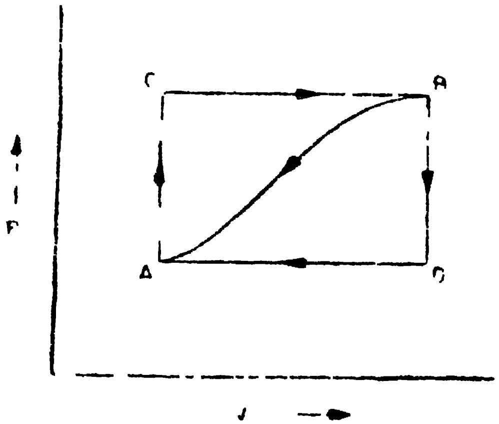


Fig 6 3

Along the path ACB,

$$H_{ACB} = U_B - U_A + W$$

Here $H = +80$ joules

$W = +30$ joules

$\therefore \quad +80 = U_B - U_A + 30$

$U_B - U_A = 80 - 30 = $ **50 joules**

(*a*) **Along the path *ADB*,**

$W = +10$ joules

$$H_{ADB} = U_B - U_A + W$$

$$H = 50+10 = \mathbf{60\ joules}$$

(*b*) For the curved path from *B* to *A*,

$$W = -20 \text{ joules}$$

$$H = (U_A - U_B) + W$$

$$= -50-20 = \mathbf{-70\ joules}$$

(—ve sign shows that heat is liberated by the system)

(*c*) $U_A = 0,\qquad U_D = 40$ joules

$$U_B - U_A = 50$$

$\therefore$ $U_B = 50$ joules

In the process *ADB*, 10 joules of work is done. Work done from *A* to *D* is +10 joules and from *D* to *B* is zero.

For *AD*,

$$H_{AD} = (U_D - U_A) + W$$

$$= 40+10 = 50 \text{ joules}$$

For *DB*

$$H_{DB} = U_C - U_D + W$$

$$= 50-40+0 = \mathbf{10\ joules}$$

6·10 Applications of First Law of Thermodynamics

Specific Heat of a Gas (*T* and *V* Independent)

The internal energy of a system is a single valued function of the state variables *viz.*, pressure, volume, temperature etc. In the case of a gas, any two of the variables *P*, *V*, *T* are sufficient to define completely its state. If *V* and *T* are chosen as the independent variables,

$$U = f(V, T) \qquad \ldots(i)$$

Differentiating equation (*i*)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad \ldots(ii)$$

If an amount of heat δH is supplied to a thermodynamical system, say an ideal gas and if the volume increases by dV at a constant pressure P, then according to the first law of thermodynamics

$$\delta H = dU + \delta W$$

Here $\delta W = P.dV$

$\therefore$ $\delta H = dU + P.dV$

Substituting the value of dU from equation (*ii*)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \qquad \ldots(iii)$$

Dividing both sides by dT

$$\frac{\delta H}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + \frac{P.dV}{dT}$$

or $$\left(\frac{\delta H}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dV}{dT} \qquad \text{...(iv)}$$

If the gas is heated at constant volume,

$$\left(\frac{\delta H}{\partial T}\right)_V = C_V$$

and $$\frac{dV}{dT} = 0$$

$$\therefore \left(\frac{\delta H}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \text{...(v)}$$

When the gas is heated at constant pressure,

$$\left(\frac{\delta H}{dT}\right)_P = C_P$$

∴ From equation (*iv*),

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

$$\therefore \quad C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

or $$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{...(vi)}$$

From Joule's experiment, for an ideal gas on opening the stop-cock, no work was done and no heat transfer took place.

So $\delta H = 0 = dU + 0$. Therefore, $dU = 0$. Even though the volume changed while the temperature is constant, there is no change in internal energy.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From the ideal gas equation

$$PV = RT$$

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

$$\therefore \; C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\therefore \; C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\therefore \; C_P - C_V = R \qquad \text{...(viii)}$$

Here C_P, C_V and R are expressed in the same units.

From equation (*iii*)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \qquad \ldots(ix)$$

For a process at constant temperature

$$dT = 0$$

$$\therefore \quad (\delta H)_T = P(dV)_T + \left(\frac{\partial U}{\partial V}\right)_T (dV)_T \qquad \ldots(x)$$

This equation represents the amount of heat energy supplied to a system in an isothermal reversible process and is equal to the sum of the work done by the system and the increase in its internal energy.

For a reversible adiabatic process

$$\delta H = 0,$$

Therefore, from equation (*ix*),

$$0 = C_V\, dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

or

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

Dividing throughout by dV,

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \ldots(xii)$$

The isobaric volume coefficient of expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \alpha V = \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \frac{C_P - C_V}{\alpha V} = P$$

$$\text{But} \left(\frac{\partial U}{\partial V}\right)_T = 0 = P - P$$

or

$$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{C_P - C_V}{\alpha V}\right) - P \qquad \ldots(xiii)$$

or

$$-\left(\frac{C_P - C_V}{\alpha V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \ldots(xiv)$$

From equations (*xii*) and (*xiv*)

$$C_V\left(\frac{\partial T}{\partial V}\right)=-\left(\frac{C_P-C_V}{\alpha V}\right)$$

or
$$\left(\frac{\partial T}{\partial V}\right)=\frac{C_V-C_P}{\alpha V C_V} \quad \ldots(xv)$$

This expression holds good for an adiabatic reversible process.

6·11 Isothermal Process

If a system is perfectly conducting to the surroundings and the temperature remains constant throughout the process, it is called

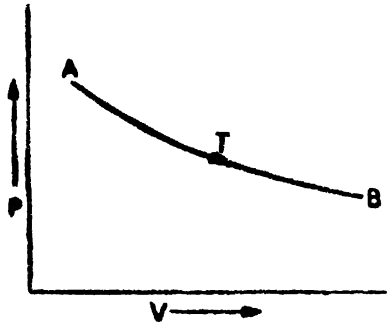


Fig. 6·4

an isothermal process. Consider a working substance at a certain pressure and temperature and having a volume represented by the point *A* (Fig [illegible]).

Pressure [illegible] decreased and work is done by the working substance at the [illegible] of its internal energy and there should be fall in temperature. [illegible], the system is perfectly conducting to the surroundings. It absorbs heat from the surroundings and maintains a constant temperature. Thus from *A* to *B* the temperature remains constant. The curve *AB* is called the *isothermal* curve or *isothermal*.

Consider the working substance at the point *B* and let the pressure be increased. External work is done on the working substance and there should be rise in temperature. But the system is perfectly conducting to the surroundings. It gives extra heat to the surroundings and its temperature remains constant from *B* to *A*.

Thus, during the isothermal process, the temperature of the working substance remains constant. It can absorb heat or give heat to the surroundings. The equation for an isothermal process is

$$PV = RT = \text{constant [For one gram molecule of a gas.]}$$

For *n* gram molecules of a gas $PV = nRT$

6·12 Adiabatic process

During an adiabatic process, the working substance is perfectly insulated from the surroundings. It can neither give heat nor take substance, there is rise in temperature because the external work done on the working substance increases its internal energy. When work is done by the working substance, it is done at the cost of its internal energy. As the system is perfectly insulated from the surroundings, there is fall in temperature.

Thus, during an adiabatic process, the working substance is perfectly insulated from the surroundings. All along the process, there is change in temperature. A curve between pressure and volume during the adiabatic process is called an adiabatic curve or an adiabatic.

Examples. 1. The compression of the mixture of oil vapour and air during compression stroke of an internal combustion is an adiabatic process and there is rise in temperature.

2. The expansion of the combustion products during the working stroke of an engine is an adiabatic process and there is fall in temperature.

3. The sudden bursting of a cycle tube is an adiabatic process.

Apply the first law of thermodynamics to an adiabatic process, $\delta H = 0$,

$$\delta H = dU + \delta W$$

or

$$0 = dU + \delta W \qquad \ldots(i)$$

The processes that take place *suddenly* or *quickly* are adiabatic processes.

6·13 Isochoric Process

If the working substance is taken in a non-expanding chamber, the heat supplied will increase the pressure and temperature. The volume of the substance will remain constant. Such a process is called an *isochoric process*. The work done is zero because there is no change in volume. The whole of the heat supplied increases the internal energy. Therefore, during the isochoric process $\delta W = 0$.

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

The heat transferred in such a process

$$\delta H = C_v dT$$

$$\therefore \qquad C_v dT = dU \qquad \ldots(ii)$$

Hence C_v is the specific heat for one gram-molecule of a gas at constant volume.

6·14 Isobaric Process

If the working substance is taken in an expanding chamber kept at a constant pressure, the process is called an isobaric process. Here, the temperature and volume change. If an amount of heat δH is given to the working substance, it is partly used in increasing the temperature of the working substance by dT and partly used in doing external work. Considering one gram of the working substance.

$$\delta H = 1 \times C_v dT + \frac{P\,.\,dV}{J} \qquad ...(i)$$

But $$\delta H = C_p.dT \qquad ...(ii)$$

$$P.dV = r.dT$$

$\therefore$ $$C_p dT = C_v.dT + \frac{r.dT}{J}$$

$$C_p - C_v = \frac{r}{J} \qquad ...(iii)$$

Here C_p and C_v represent the specific heats for 1 gram of a gas and r is the ordinary gas constant.

If C_p and C_v are the gram-molecular specific heats of gas, then

$$C_p - C_v = \frac{R}{J} \qquad ...(iv)$$

Here R is the universal gas constant.

6·15 Gas Equation During an Adiabatic Process

Consider 1 gram of the working substance (ideal gas) perfectly insulated from the surroundings. Let the external work done by the gas be δW.

Applying the first law of thermodynamics

$$\delta H = dU + \delta W$$

But $$\delta H = 0$$

and $$\delta W = P.dV$$

where P is the pressure of the gas and dV is the change in volume.

$\therefore$ $$0 = dU + \frac{P.dV}{J} \qquad ...(i)$$

As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by dT.

$$dU = 1 \times C_v \times dT$$

$$C_v.dT + \frac{P.dV}{J} = 0 \qquad ...(ii)$$

For an ideal gas

$$PV = rT \qquad ...(iii)$$

Differentiating,

$$P.dV + V.dP = r{\cdot}dT$$

Substituting the value of dT in equation (*ii*),

$$C_v \left[\frac{P.dV + V.dP}{r}\right] + \frac{P.dV}{J} = 0$$

$$C_v[P.dV + V.dP] + r.\frac{P.dV}{J} = 0$$

But. $$\frac{r}{J} = C_p - C_v$$

$$\therefore \quad C_v.P.dV+C_v.V.dP+C_p.PdV-C_vPdV = 0$$

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

Dividing by $C_v.PV$,

$$\frac{C_p}{C_v} \cdot \frac{dV}{V}+\frac{dP}{P} = 0$$

But $$\frac{C_p}{C_v} = \gamma$$

$$\therefore \quad \frac{dP}{P}+\gamma \frac{dV}{V} = 0$$

Integrating, $\log P+\gamma \log V = \text{const.}$

$$\log PV^{\gamma} = \text{const.}$$

or $$PV^{\gamma} = \text{const.} \qquad ...(iv)$$

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

Taking $$PV = rT$$

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

$$\left(\frac{rT}{V}\right). V^{\gamma} = \text{const.}$$

But r is const.

$$rTV^{\gamma-1} = \text{const.}$$

$$\therefore \quad TV^{\gamma-1} = \text{const.} \qquad ...(v)$$

Also $$V = \frac{rT}{P}$$

$$P\left[\frac{rT}{P}\right]^{\gamma} = \text{const.}$$

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

or $$\frac{P^{\gamma-1}}{T^{\gamma}} = \text{const.} \qquad ...(vi)$$

Thus, during an adiabatic process

(*i*) $PV^{\gamma} = \text{const.}$

(*ii*) $TV^{\gamma-1} = \text{const.}$ and

(*iii*) $\dfrac{P^{\gamma-1}}{T^{\gamma}} = \text{const.}$

Example 6·2. *A motor car tyre has a pressure of 2 atmospheres at the room temperature of 27°C. If the tyre suddenly bursts, find the resulting temperature.*

Here,

$$\begin{aligned}
P_1 &= 2 \text{ atmospheres} \\
T_1 &= 273+27 \\
&= 300 \text{ K} \\
P_2 &= 1 \text{ atmosphere} \\
T_2 &= ? \\
\gamma &= 1{\cdot}4 \\
\frac{P_1^{\gamma-1}}{T_1^{\gamma}} &= \frac{P_2^{\gamma-1}}{T_2^{\gamma}} \\
\left(\frac{P_2}{P_1}\right)^{\gamma-1} &= \left(\frac{T_2}{T_1}\right)^{\gamma} \\
\left(\frac{1}{2}\right)^{0.4} &= \left(\frac{T_2}{300}\right)^{1.4} \\
0{\cdot}4 \log (0.5) &= 1{\cdot}4\,[\log T_2 - \log 300] \\
-0{\cdot}1204 &= 1{\cdot}4 \log T_2 - 3{\cdot}4680 \\
1{\cdot}4 \log T_2 &= 3{\cdot}4680 - 0{\cdot}1204 \\
&= 3{\cdot}3476 \\
\log T_2 &= \frac{3{\cdot}3476}{1{\cdot}4} \\
&= 2{\cdot}3911 \\
T_2 &= 246{\cdot}1 \text{ K} \\
&= -26{\cdot}9^\circ\text{C}
\end{aligned}$$

Example 6·3. *A quantity of air at 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the final (i) pressure and (ii) temperature.*

(*i*) $P_1 = 1$ atmosphere ; $P_2 = ?$, $\gamma = 1{\cdot}4$

$V_1 = V$; $V_2 = \frac{V}{2}$

During sudden compression, the process is adiabatic

$$\begin{aligned}
P_1V_1^{\gamma} &= P_2V_2^{\gamma} \\
P_2 &= P_1\left[\frac{V_1}{V_2}\right]^{\gamma} \\
&= 1[2]^{1.4} \\
&= 2{\cdot}636 \text{ atmospheres}
\end{aligned}$$

(*ii*) $V_1 = V$; $V_2 = \frac{V}{2}$

$$\begin{aligned}
T_1 &= 300 \text{ K} ; T_2 = ? \\
\gamma &= 1{\cdot}4 \\
T_1(V_1)^{\gamma-1} &= T_2\,(V_2)^{\gamma-1} \\
T_2 &= T_1[2]^{1.4-1} \\
&= 300[2]^{0.4} \\
&= 395{\cdot}9 \text{ K} \\
&= 122{\cdot}9^\circ\text{C}
\end{aligned}$$

Example 6 4. *Air is compressed adiabatically to half its volume. Calculate the change in its temperature.* *(Delhi 1969)*

Let the initial temperature be T_1 K and the final temperature T_2 K.

Initial volume $= V_1$

Final volume $= V_2$

$= \frac{V_1}{2}$

During an adiabatic process

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$T_2 = T_1[2]^{\gamma-1}$$

But γ for air $= 1\cdot40$

$$T_2 = T_1[2]^{1\cdot40-1}$$

$$T_2 = T_1[2]^{0\cdot40}$$

$$T_2 = 1\cdot319\,T_1$$

Change in temperature

$$= T_2-T_1$$

$$= 1\cdot319\,T_1-T_1$$

$$= \mathbf{0\cdot319\ T_1\ K}$$

Example 6 5 *1 gram molecule of a monoatomic ($\gamma = 5/3$) perfect gas at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmospheres. Calculate the resulting difference in temperature.*

[Delhi (Hons.) 1973]

In a reversible adiabatic process

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

or

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

Here, $P_2 = 50$,

$P_1 = 1$,

$T_1 = 273+27$

$= 300$ K

$T_2 = ?$

$\gamma = \frac{5}{3}$

$$\therefore \quad (50)^{2/3} = \left(\frac{T_2}{300}\right)^{5/3}$$

or

$$\frac{2}{3}\log(50) = \frac{5}{3}[\log T_2-\log 300]$$

$$T_2 = \mathbf{1{,}434\ K}$$

$$= \mathbf{1{,}161°C}$$

Example 6·6. *A quantity of dry air at 27°C is compressed (i) slowly and (ii) suddenly to 1/3 of its volume. Find the change in temperature in each case, assuming γ to be 1·4 for dry air.*

[*Agra 1969 ; Delhi 71, 75*]

(1) When the process is slow, the temperature of the system remains constant. Therefore, there is no change in temperature.

(2) When the compression is sudden, the process is adiabatic.

Here $V_1 = V, \quad V_2 = \frac{V}{3}$

$$T_1 = 300\text{ K}, \quad T_2 = ?$$

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

$$T_2\,(V_2)^{\gamma-1} = T_1\,[V_1]^{\gamma-1}$$

$$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

or $$T_2 = 300\left[\frac{3V}{V}\right]^{\gamma-1}$$

$$= 300\,[3]^{1{\cdot}4-1}$$

or $$T_2 = 465{\cdot}5\text{ K}$$

$$= 192{\cdot}5\ ^\circ\text{C}$$

The temperature of air increases by

$$192{\cdot}5 - 27 = \mathbf{165{\cdot}5\ ^\circ C} \quad \text{or} \quad \mathbf{165{\cdot}5\ K}$$

Example 6·7. *A certain mass of gas at* NTP *is expanded to three times its volume under adiabatic conditions. Calculate the resulting temperature and pressure. γ for the gas is 1·40.*

[*Delhi (Hons.) 75*]

(1) Here, $V_1 = V, \quad V_2 = 3V$

$$T_1 = 273\text{ K} \quad T_2 = ?$$

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

or $$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$T_2 = 273\left[\frac{1}{3}\right]^{1{\cdot}4-1}$$

$$T_2 = \mathbf{176\ K} = \mathbf{-97^\circ C}$$

(2) Here, $V_1 = V, \quad V_2 = 3V$

$$P_1 = 1\text{ atmosphere}, \quad P_2 = ?$$

$$P_1\,V_1^{\gamma} = P_2\,V_2^{\gamma}$$

$$P_2 = P_1\left[\frac{V_1}{V_2}\right]^{\gamma}$$

$$P_2 = 1\left(\frac{1}{3}\right)^{1{\cdot}4}$$

$$P_2 = 0{\cdot}2148\text{ atmosphere}$$

6·16 Slopes of Adiabatics and Isothermals

In an isothermal process

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

Differentiating,

$$PdV+VdP = 0$$

or

$$\frac{dP}{dV} = -\frac{P}{V} \qquad ..(i)$$

In an adiabatic process

$$PV^{\gamma} = \text{const.}$$

Differentiating,

$$P\gamma V^{\gamma-1}\, dV+VdP = 0$$

$$\frac{dP}{dV} = -\frac{\gamma P}{V} \qquad ...(ii)$$

Therefore, the slope of an adiabatic is γ times the slope of the isothermal.

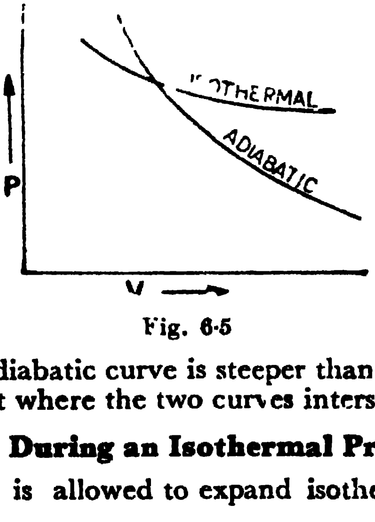


Fig. 6·5

Hence, the adiabatic curve is steeper than the isothermal curve (Fig. 6·5) at a point where the two curves intersect each other.

6·17 Work Done During an Isothermal Process

When a gas is allowed to expand isothermally, work is done by it.

Let the initial and final volumes be V_1 and V_2 respectively. In Fig. 6·6, the area of the shaded strip represents the work done for a small change in volume dV. When the volume changes from V_1 to V_2,

$$\text{Work done} = \int_{V_1}^{V_2} P\,.\,dV = \text{area } ABba \qquad ...(i)$$

Fig. 6·6 represents the indicator diagram. Considering one gram molecule of the gas

$$PV = RT$$

or

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

$$\therefore \qquad W = RT\int_{V_1}^{V_2}\frac{dV}{V}$$

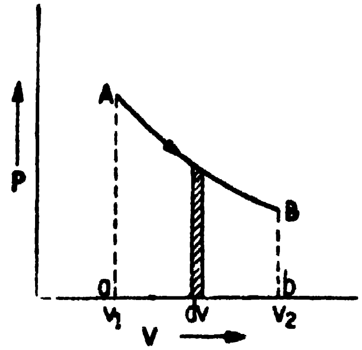


Fig. 6·6

$$= RT\log_e\frac{V_2}{V_1} \qquad (ii)$$

$$W = RT \times 2.3026\log_{10}\frac{V_2}{V_1} \qquad (iii)$$

Also $\qquad P_1V_1 = P_2V_2$

or $$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W = RT \times 2.3026\log_{10}\frac{P_1}{P_2} \qquad (iv)$$

Here the change in the internal energy of the system is zero (because the temperature remains constant). So the heat transferred is equal to the work done.

6.18 Work Done During an Adiabatic Process

During an adiabatic process, the gas expands from volume V_1 to V_2. As shown by the indicator diagram (Fig. 6.7) the work done for an increase in

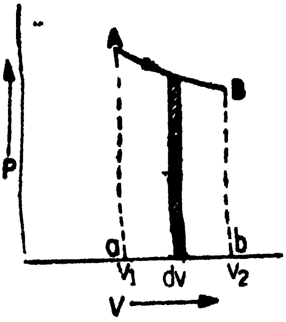


Fig. 6.7

volume $dV = P\,dV$. Work done when the gas expands from V_1 to V_2 is given by,

$$W = \int_{V_1}^{V_2} PdV = \text{Area } ABba$$

During an adiabatic process,

$$PV^{\gamma} = \text{const} = K$$

or
$$P = \frac{K}{V^{\gamma}}$$

$$W = K\int_{V_1}^{V_2}\frac{dV}{V^{\gamma}}$$

$$= \frac{1}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right] \qquad \text{...(i)}$$

Since A and B lie on the same adiabatic

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

$$W = \frac{1}{1-\gamma}\left[\frac{K}{V_2^{\gamma-1}} - \frac{K}{V_1^{\gamma-1}}\right]$$

$$W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] \qquad \text{...(ii)}$$

Taking T_1 and T_2 as the temperatures at the points A and B respectively and considering one gram molecule of the gas

$$P_1V_1 = RT_1$$

and
$$P_2V_2 = RT_2$$

Substituting these values in equation (*ii*)

$$W = \frac{1}{1-\gamma}\left[RT_2 - RT_1\right] \qquad \text{...(iii)}$$

Here, heat transferred is zero because the system is thermally insulated from the surroundings. The decrease in the internal energy of the system (due to fall in temperature) is equal to the work done by the system and *vice versa*.

6·19. Relation Between Adiabatic and Isothermal Elasticities

1. Isothermal Elasticity

During an isothermal process

$$PV = \text{const}$$

Differentiating,

$$PdV + VdP = 0$$

or
$$\frac{V.dP}{-dV} = P \qquad \text{...(i)}$$

From the definition of elasticity of a gas

$$E_{iso} = \frac{dP}{-dV/V}$$

$$= \frac{VdP}{-dV} \qquad \text{...(ii)}$$

From (*i*) and (*ii*)

$$E_{iso} = P \qquad \text{...}(iii)$$

2. Adiabatic Elasticity

During an adiabatic process

$$PV^{\gamma} = \text{const}$$

Differentiating, $P\gamma V^{\gamma-1}dV + V^{\gamma}dP = 0$

or

$$\frac{VdP}{-dV} = \gamma P \qquad \text{...}(iv)$$

From the definition of elasticity of a gas

$$E_{adi} = \frac{dP}{-dV/V}$$

$$= \frac{V.dP}{-dV} \qquad \text{...}(v)$$

From (*iv*) and (*v*),

$$E_{adi} = \gamma P \qquad \text{...}(vi)$$

Comparing (*iii*) and (*vi*)

$$E_{adi} = \gamma E_{iso}$$

Thus, the adiabatic elasticity of a gas is γ times the isothermal elasticity.

6·20 Clement and Desormes Method—Determination of γ

Clement and Desormes in 1819 designed an experiment to find γ, the ratio between the two specific heats of a gas.

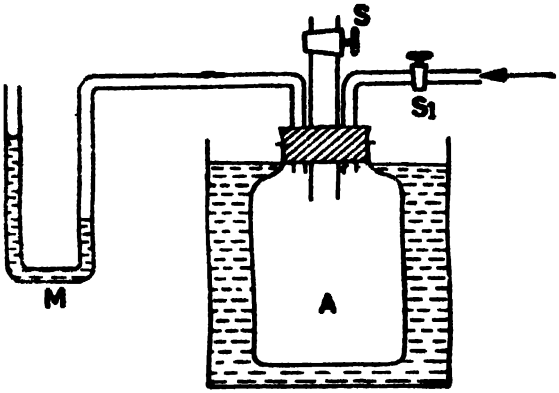


Fig. 6·8

The vessel A has a capacity of 20 to 30 litres and is fitted in a box containing cotton and wool. At the top end, three tubes are fitted as shown in Fig. 6·8. Through S_1, dry air is forced into the vessel A. The stop cock S_1 is closed when the pressure inside A is slightly greater than the atmospheric pressure. Let the difference in level on the two sides of the manometer be H and the atmospheric pressure be P_0. The pressure of air inside the vessel is P_1.

The stop-cock S is suddenly opened and closed just at the moment when the levels of the liquid on the two sides of the manometer are the same. Some quantity of air escapes to the atmosphere. The air inside the vessel expands adiabatically. The temperature of air inside the vessel falls due to adiabatic expansion. The air inside the vessel is allowed to gain heat from the surroundings and it finally attains the temperature of the surroundings. Let the pressure at the end be P_2 and the difference in levels on the two sides of the manometer be h.

Theory. Consider a fixed mass of air left in the vessel in the end. This mass of air has expanded from volume V_1 (less than the volume of the vessel) at pressure P_1 to volume V_2 at pressure P_0. The process is adiabatic as shown by the curve AB (Fig. 6·9).

$$P_1V_1^{\gamma} = P_0V_2^{\gamma}$$

$$\frac{P_1}{P_0} = \left(\frac{V_2}{V_1}\right)^{\gamma} \qquad \ldots(i)$$

Finally the point C is reached. The points A and C are at the room temperature. Therefore AC can be considered as an isothermal.

$$P_1V_1 = P_2V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \qquad \ldots(ii)$$

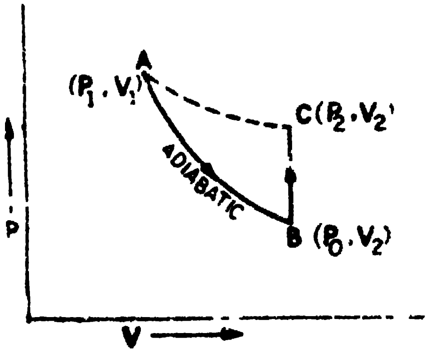


Fig. 6·9

Substituting the value of $\frac{V_2}{V_1}$ in equation (*i*),

$$\frac{P_1}{P_0} = \left(\frac{P_1}{P_2}\right)^{\gamma}$$

Taking logarithms.

$$\log P_1 - \log P_0 = \gamma(\log P_1 - \log P_2)$$

$$\gamma = \frac{\log P_1 - \log P_0}{\log P_1 - \log P_2} \qquad \ldots(iii)$$

But $$P_1 = P_0+H \text{ and } P_2 = P_0+h$$

$\therefore$ $$\gamma = \frac{\log(P_0+H)-\log P_0}{\log(P_0+H)-\log(P_0+h)}$$

$$\gamma = \frac{\log\left(\frac{P_0+H}{P_0}\right)}{\log\left(\frac{P_0+H}{P_0+h}\right)}$$

$$= \frac{\log\left(1+\frac{H}{P_0}\right)}{\log\left(1+\frac{H-h}{P_0+h}\right)}$$

Approximately, $$\gamma = \frac{\frac{H}{P_0}}{\frac{H-h}{P_0}} = \frac{H}{H-h}$$

Hence $$\gamma = \frac{H}{H-h} \qquad \ldots(ii)$$

Similarly, γ for any gas can be determined by this method.

Drawbacks. When the stop-cock is opened, a series of oscillations are set up. This is shown by the up and down movement of the liquid in the manometer. Therefore, the exact moment when the stopcock should be closed is not known. The pressure may not be equal to the atmospheric pressure when the stop-cock is closed. It may be higher or less than the atmospheric pressure. Thus the result obtained will not be accurate.

6·21 Partington's Method

Lummer, Pringsheim and Partington designed an apparatus to determine the value of γ. In this method, the pressure and temperature are measured accurately before and after the adiabatic expansion.

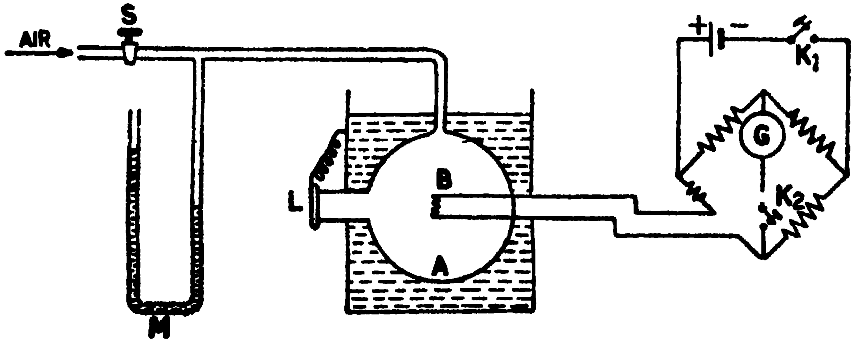


Fig. 6·10

The apparatus consists of a vessel A having a capacity between 130 and 150 litres. The valve L can be opened and closed suddenly.

It is controlled by a spring arrangement (Fig. 6 10). Dry air (or gas) at a pressure higher than the atmospheric pressure is forced into the vessel A and the stop cock S is closed. The oil manometer M is used to measure the pressure of air inside the vessel A. The bolometer B (a platinum wire) and a sensitive galvanometer are used in the Wheatstone's bridge arrangement.

The vessel is surrounded by a constant temperature bath. Let the initial pressure and temperature be P_1 and T_1 (room temperature). The bridge is kept slightly disturbed from the balanced position. The valve L is suddenly opened and closed. The Wheatstones bridge is at once adjusted for balanced position. The temperature of air inside A has decreased due to adiabatic expansion of air. Let the temperature inside be T_0 and the atmospheric pressure P_0. If the apparatus is allowed to remain as such for some time, it will gain heat from the surroundings and the balance point gets disturbed. In order that the balance point remains undisturbed, some pieces of ice are added into the water surrounding the vessel A. When the temperature of water bath is the same as that of air just after adiabatic expansion, the bridge will remain balanced.

The temperature T_0 of the bath represents the temperature of air after the adiabatic expansion.

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_0^{\gamma-1}}{T_0^{\gamma}}$$

$$\left(\frac{P_1}{P_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{\gamma}$$

$$(\gamma-1)(\log P_1-\log P_0) = \gamma\,[\log T_1-\log T_0]$$

$$\gamma = \frac{\log P_1-\log P_0}{(\log P_1-\log P_0)-(\log T_1-\log T_0)}$$

As P_1, P_0, T_1 and T_0 are known, γ can be calculated. The value of γ for air at 17°C is found to be 1·4034.

Advantages. (1) Due to the large volume of the vessel, the expansion is adiabatic.

(2) The temperatures are measured accurately just before and after the adiabatic expansion.

Drawbacks. This method cannot be used to find the value of γ at higher temperatures because it is not possible to determine the cooling correction accurately.

6·22 Ruchhardt's Experiment

In 1929, Ruchhardt designed an apparatus to find the value of γ. It is based on the principle of mechanics. Air (or gas) is enclosed in a big jar (Fig. 6·11). A tube of uniform area of cross section is fitted and a ball of mass m fits in the tube just like a piston. In the equilibrium position, the ball is at the point A. The pressure P of air inside the vessel, is given by

$$P = P_0 + \frac{mg}{A}$$

where P_0 is the atmospheric pressure and A is the area of cross-section of the tube.

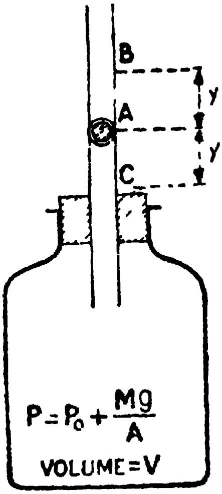


Fig. 6·11

The ball is given a small downward movement through a distance y. It moves up and down and executes simple harmonic motion. Let the change in volume be dV and change in pressure be dP.

$$dV = yA$$

and $$dP = \frac{F}{A}$$

where F is the restoring force

As the ball moves quite rapidly, the process of change in P and V is adiabatic.

$\therefore$ $$PV^{\gamma} = \text{const}$$

Differentiating, $P\gamma V^{\gamma-1}\,dV + V^{\gamma}.\,dP = 0$

$$\gamma PdV + VdP = 0$$

Substituting the values of dV and dP,

$$\gamma PyA + \frac{V}{A}.F = 0,$$

But $$F = M\,.\frac{d^2y}{dt^2}$$

or $$F = -\frac{\gamma PA^2}{V}\,.\,y \qquad \text{...}(i)$$

$$\therefore \quad \frac{d^2y}{dt^2} + \frac{\gamma PA^2}{VM}\,.y = 0 \qquad \text{...}(ii)$$

Equation (*ii*) represents S.H.M.

Let the time period be t

$$t = 2\pi\sqrt{\frac{\text{displacement}}{\text{acceleration}}}$$

$$= 2\pi\sqrt{\frac{y}{-d^2y/dt^2}}$$

$$t = 2\pi\sqrt{\frac{VM}{\gamma PA^2}}$$

$$\gamma = \frac{4\pi^2 VM}{PA^2t^2} \qquad \ldots(iii)$$

As V, M, P and A are already known, only the time period t is to be determined.

Hence γ can be calculated.

This experiment is not very accurate because the ball comes to rest in a short time due to friction and the time period cannot be determined accurately.

Rinkle's Modification. Rinkle suggested a modification in Ruchhardt's experiment. The ball is kept in the equilibrium position where the pressure of air (or gas) is exactly equal to the atmospheric pressure. The ball is allowed to drop and the distance L through which it drops before starting to move up again is noted. This distance is found accurately by taking a series of photographs of the moving ball.

$$\text{Work done} = \int_0^L F \,.\, dy$$

But

$$F = \frac{\gamma P_0 A^2 y}{V}$$

$$W = \frac{\gamma P_0 A^2}{V}\int_0^L y\,dy$$

$$= \frac{\gamma P_0 A^2 L^2}{2V} \qquad \ldots(iv)$$

$$\text{Work done} = MgL \qquad \ldots(v)$$

Equating (iv) and (v)

$$\frac{\gamma P_0 A^2 L^2}{2V} = MgL$$

$$\gamma = \frac{2MgV}{P_0 A^2 L} \qquad \ldots(vi)$$

As M, g, V, P_0 and A are known, L is measured from the photographic film. Hence γ can be calculated. The error in the result is due to the following assumptions : (i) that there is no friction, (ii) that the gas is ideal and (iii) the process is completely adiabatic.

6·23 Irreversible Process

The thermodynamical state of a system can be defined with the help of the thermodynamical coordinates of the system. The state of a system can be changed by altering the thermodynamical coordinates. Changing from one state to the other by changing the thermodynamical coordinates is called a *process*.

Consider two states of a system *i.e.*, state A and state B. Change of state from A to B or *vice versa* is a process and the direction of the process will depend upon a new thermodynamical coordinate called **entropy**. All processes are not possible in the universe.

Consider the following processes :

(1) Let two blocks A and B at different temperatures T_1 and T_2 $(T_1 > T_2)$ be kept in contact but the system as a whole is insulated from the surroundings. Conduction of heat takes place between the blocks, the temperature of A falls and the temperature of B rises and thermodynamical equilibrium will be reached.

(2) Consider a fly wheel rotating with an angular velocity ω. Its initial kinetic energy is $\frac{1}{2}I\omega^2$. After some time the wheel comes to rest and kinetic energy is utilised in overcoming friction at the bearings. The temperature of the wheel and the bearings rise and the increase in their internal energy is equal to the original kinetic energy of the fly wheel.

(3) Consider two flasks A and B connected by a glass tube provided with a stop cock. Let A contain air at high pressure and B is evacuated. The system is isolated from the surroundings. If the stop cock is opened, air rushes from A to B, the pressure in A decreases and the volume of air increases.

All the above three examples though different are thermodynamical processes involving change in thermodynamical coordinates. Also, in accordance with the first law of thermodynamics, the principle of conservation of energy is not violated because the total energy of the system is conserved. It is also clear that, with the initial conditions described above, the three processes will take place.

Let us consider the possibility of the above three processes taking place in the reverse direction. In the first case, if the reverse process is possible, the block B should transfer heat to A and initial conditions should be restored. In the second case, if the reverse process is possible, the heat energy must again change to kinetic energy and the fly wheel should start rotating with the initial angular velocity ω. In the third case, *if the reverse process is possible* the air in B must flow back to A and the initial condition should be obtained.

But, it is a matter of common experience, that none of the above conditions for the reverse processes are reached. It means that the direction of the process cannot be determined by knowing the thermodynamical coordinates in the two end states. To determine the direction of the process a new thermodynamical coordinate has been devised by Clausius and this is called the entropy of the system. Similar to internal energy, entropy is also a function of the state of a system. For any possible process, the entropy of an isolated system should increase or remain constant. The process in which there is a possibility of decrease in entropy cannot take place.

If the entropy of an isolated system is maximum, any change of state will mean decrease in entropy and hence that change of state will not take place.

To conclude, ***processes in which the entropy of an isolated system decreases do not take place or for all processes taking place in an isolated system the entropy of the system should increase or remain constant.*** It means a process is irreversible if the entropy decreases when the direction of the process is reversed. A process is said to be irreversible if it cannot be retraced back exactly in the opposite direction. During an irreversible process, heat energy is always used to overcome friction. Energy is also dissipated in the form of conduction and radiation. This loss of energy always takes place whether the engine works in one direction or the reverse direction. Such energy cannot be regained. In actual practice all the engines are irreversible. If electric current is passed through a wire, heat is produced. If the direction of the current is reversed, heat is again produced. This is also an example of an irreversible process. All chemical reactions are irreversible. In general, all natural processes are irreversible.

6 24 Reversible Process

From the thermodynamical point of view, a reversible process is one in which an infinitesimally small change in the external conditions will result in all the changes taking place in the direct process but exactly repeated in the reverse order and in the opposite sense. The process should take place at an extremely slow rate. In a reversible cycle, there should not be any loss of heat due to friction or radiation. In this process, the initial conditions of the working substance can be obtained.

Consider a cylinder containing a gas at a certain pressure and temperature. The cylinder is fitted with a frictionless piston. If the pressure is decreased, the gas expands slowly and maintains a constant temperature (isothermal process). The energy required for this expansion is continuously drawn from the source (surroundings). If the pressure on the piston is increased, the gas contracts slowly and maintains constant temperature (isothermal process). The energy liberated during compression is given to the sink (surroundings). This is also true for an adiabatic process provided the process takes place infinitely slowly.

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

The conditions of reversibility for any heat engine or process can be stated as follows :—

(1) The pressure and temperature of the working substance

must not differ appreciably from those of the surroundings at any stage of the cycle of operation.

(2) All the processes taking place in the cycle of operation must be infinitely slow.

(3) The working parts of the engine must be completely free from friction.

(4) There should not be any loss of energy due to conduction or radiation during the cycle of operation.

It should be remembered that the complete reversible process or cycle of operation is only an ideal case. In an actual process, there is always loss of heat due to friction, conduction or radiation. The temperature and pressure of the working substance differ appreciably from those of the surroundings.

6 25 Second Law of Thermodynamics

A heat engine is chiefly concerned with the conversion of heat energy into mechanical work. A refrigerator is a device to cool a certain space below the temperature of its surroundings. The first law of thermodynamics is a qualitative statement which does not preclude the possibility of the existence of either a heat engine or a refrigerator. The first law does not contradict the existence of a 100% efficient heat engine or a self-acting refrigerator.

In practice, these two are not attainable. These phenomena are recognized and this led to the formulation of a law governing these two devices. It is called second law of thermodynamics.

A new term reservoir is used to explain the second law. A **reservoir** is a device having infinite thermal capacity and which can absorb, retain or reject unlimited quantity of heat without any change in its temperature.

Kelvin-Planck statement of the second law is as follows :

"It is impossible to get a continuous supply of work from a body (or engine) which can transfer heat with a single heat reservoir. This is a negative statement. According to this statement, a single reservoir at a single temperature cannot continuously transfer heat into work. It means that there should be two reservoirs for any heat engine. One reservoir (called the source) is taken at a higher temperature and the other reservoir (called the sink) is taken at a lower temperature.

According to this statement, zero degree absolute temperature is not attainable because no heat is rejected to the sink at zero degree Kelvin. If an engine works between any temperature higher than zero degree Kelvin and zero degree Kelvin, it means it uses a single reservoir which contradicts Kelvin-Planck's statement of the second law. Similarly, no engine can be 100% efficient.

In a heat engine, the engine draws heat from the source and after doing some external work, it rejects the remaining heat to the sink. The source and sink are of infinite thermal capacity and they maintain constant temperature.

First Part. According to Kelvin, the second law can also be stated as follows :

"It is impossible to get a continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings".

In a heat engine the working substance does some work and rejects the remaining heat to the *sink*. The temperature of the source must be higher than the surroundings and the engine will not work when the temperatures of the source and the sink are the same. Take the case of a steam engine. The steam (working substance) at high pressure is introduced into the cylinder of the engine. Steam expands, and it does external work. The contents remaining behind after doing work are rejected to the surroundings The temperature of the working substance rejected to the surroundings is higher than the temperature of the surroundings.

If this working substance rejected by the first engine is used in another engine, it can do work and the temperature of the working substance will fall further.

It means that the working substance can do work only if its temperature is higher than that of the surroundings.

Second Part. According to Clausius :

'It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance"

This part is applicable in the case of ice plants and refrigerators Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature But, it is possible, if some external work is done on the working substance. Take the case of ammonia ice plant Ammonia is the working substance Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted to low pressure vapour. External work is done to compress the ammonia vapours to high pressure This ammonia at high pressure is passed through coils over which water at room temperature is poured. Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature) This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

Thus, the second law of thermodynamics plays an important part for practical devices *e.g.*, heat engines and refrigerators. The first law of thermodynamics only gives the relation between the work done and the heat produced. But the second law of thermodynamics gives the conditions under which heat can be converted into work.

6·25 Carnot's Reversible Engine

Heat engines are used to convert heat into mechanical work. Sadi Carnot (French) conceived a theoretical engine which is free from all the defects of practical engines. Its efficiency is maximum and it is an ideal heat engine.

For any engine, there are three essential requisites.

(1) **Source.** The source should be at a fixed high temperature T_1 from which the heat engine can draw heat. It has infinite thermal capacity and any amount of heat can be drawn from it at constant temperature T_1.

(2) **Sink.** The sink should be at a fixed lower temperature T_2 to which any amount of heat can be rejected. It also has infinite thermal capacity and its temperature remains constant at T_2.

(3) **Working Substance.** A cylinder with non conducting sides and conducting bottom contains the perfect gas as the *working substance*.

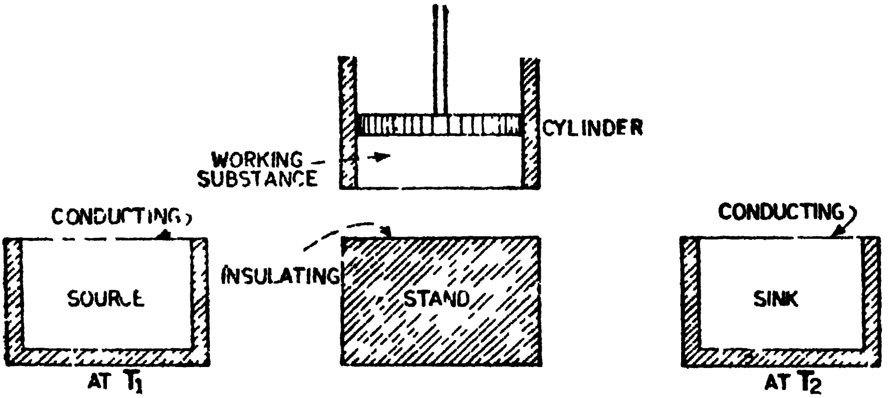


Fig. 6·12

A perfect non conducting and frictionless piston is fitted into the cylinder. The working substance undergoes a complete cyclic operation (Fig. 6·12).

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

Carnot's Cycle

(1) Place the engine containing the working substance over the source at temperature T_1. The working substance is also at a temperature T_1. Its pressure is P_1 and volume is V_1 as shown by the point A in Fig. 6·13. Decrease the pressure. The volume of the working substance increases. Work is done by the working substance. As the bottom is perfectly conducting to the source at temperature T_1, it absorbs heat. The process is completely isothermal. The temperature remains constant. Let the amount of heat

absorbed by the working substance be H_1 at the temperature T_1. The point B is obtained.

Consider one gram molecule of the working substance.

Work done from A to B (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P.\,dV = RT_1 \log \frac{V_2}{V_1}$$

$$= \text{area } ABGE \qquad \ldots(i)$$

(2) Place the engine on the stand having an insulated top. Decrease the pressure on the working substance. The volume increases. The process is completely adiabatic. Work is done by the working substance at the cost of its internal energy. The temperature falls. The working substance undergoes adiabatic change from B to C. At C the temperature is T_2 (Fig. 6·13).

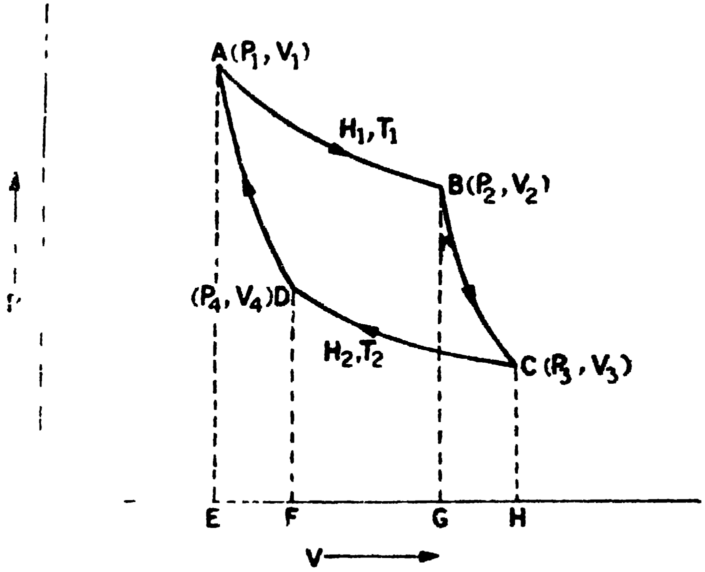


Fig. 6·13

Work done from B to C (adiabatic process)

$$W_2 = \int_{V_2}^{V_3} P\,.\,dV$$

$$= \int_{V_2}^{V_3} \frac{K\,dV}{V^\gamma}$$

$$= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma}$$

$$= \frac{P_3V_3 - P_2V_2}{1-\gamma}$$

$$= \frac{R[T_2 - T_1]}{1-\gamma} = \frac{R[T_1 - T_2]}{\gamma - 1}$$

But $PV^\gamma = \text{constant} = K$

$$P_2V_2 = RT_1$$

$$P_3V_3 = RT_2$$

$$P_3V_3^\gamma = P_2V_2^\gamma = K$$

$$W_2 = \text{Area } BCHG \qquad \ldots(ii)$$

(3) Place the engine on the sink at temperature T_2. Increase the pressure. The work is done on the working substance. As the base is conducting to the sink, the process is isothermal. A quantity of heat H_2 is rejected to the sink at temperature T_2. Finally the point D is reached.

Work done from C to D (isothermal process)

$$W_3 = \int_{V_3}^{V_4} PdV$$

$$= RT_2 \log \frac{V_4}{V_3}$$

$$= -RT_2 \log \frac{V_3}{V_4} \qquad \text{...}(iii)$$

$$W_3 = \text{area } CHFD$$

(The —ve sign indicates that work is done on the working substance.)

(4) Place the engine on the insulating stand. Increase the pressure. The volume decreases. The process is completely adiabatic. The temperature rises and finally the point A is reached.

Work done from D to A (adiabatic process).

$$W_4 = \int_{V_4}^{V_1} PdV$$

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

$$W_4 = \text{Area } DFEA \qquad \text{...}(iv)$$

[W_2 and W_4 are equal and opposite and cancel each other.]

The net work done by the working substance in one complete cycle

$$= \text{Area } ABGE + \text{Area } BCHG - \text{Area } CHFD - \text{Area } DFEA$$

$$= \text{Area } ABCD$$

The net amount of heat absorbed by the working substance

$$= H_1 - H_2$$

$$\text{Net work} = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \log\frac{V_2}{V_1} + \frac{R(T_1-T_2)}{\gamma-1} - RT_2 \log \frac{V_3}{V_4} - \frac{R[T_1-T_2]}{\gamma-1}$$

$$W = RT_1 \log\frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \qquad \text{...}(v)$$

The points A and D are on the same adiabatic

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

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

The points B and C are on the same adiabatic

$$T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$$

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

From (*vi*) and (*vii*)

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

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

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

From equation (*v*)

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

$$W = R\left[\log\frac{V_2}{V_1}\right]\left[T_1 - T_2\right]$$

$\therefore$
$$W = H_1 - H_2$$

Efficiency
$$\eta = \frac{\text{Useful output}}{\text{Input}} = \frac{W}{H_1}$$

Heat is supplied from the source from A to B only.

$$H_1 = RT_1 \log \frac{V_2}{V_1}$$

$\therefore$
$$\eta = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}$$

$$= \frac{R[T_1 - T_2] \log\left(\frac{V_2}{V_1}\right)}{RT_1 \log\left(\frac{V_2}{V_1}\right)}$$

or
$$\eta = 1 - \frac{H_2}{H_1}$$

$$\eta = 1 - \frac{T_2}{T_1} \qquad \ldots(viii)$$

The Carnot's engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The heat H_2 is taken from the sink and external work is done on the working substance and heat H_1 is given to the source at a higher temperature.

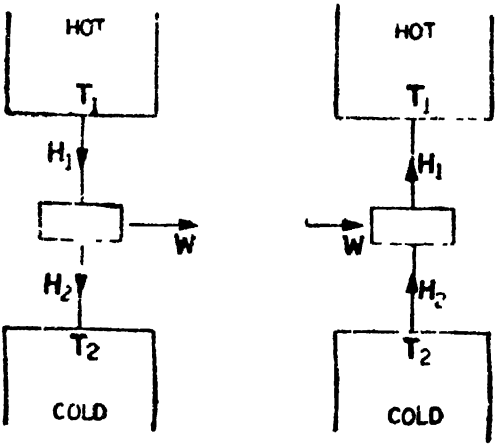
The isothermal process will take place only when the piston moves very slowly to give enough time for the heat transfer to take place. The adiabatic process will take place when the piston moves extremely fast to avoid heat transfer. Any practical engine cannot satisfy these conditions.

All practical engines have an efficiency less than the Carnot's engine.

6·27 Carnot's Engine and Refrigerator

Carnot's cycle is perfectly reversible. It can work as a heat engine and also as a refrigerator. When it works as a heat engine, it absorbs a quantity of heat H_1 from the source at a temperature T_1, does an amount of work W and rejects an amount of heat H_2 to the sink at temperature T_2. When it works as a refrigerator, it absorbs heat H_2 from the sink at temperature T_2. W amount of work is done on it by some external means and rejects heat H_1 to the source at a temperature T_1 (Fig. 6·14) In the second case heat flows from a body at a lower temperature to a body at a higher temperature, with the help of external work done on the working substance and it works as a refrigerator This will not be possible if the cycle is not completely reversible

Coefficient of Performance The amount of heat absorbed at the lower temperature is H_2. The amount of work done by the external process (input energy) = W and the amount of heat rejected = H_1 Here H_2 is the desired refrigerating effect.



(i) HEAT ENGINE

(ii) REFRIGERATOR

Fig. 6·14

Coefficient of performance

$$= \frac{H_2}{W} = \frac{H_2}{H_1-H_2}$$

Suppose 200 joules of energy is absorbed at the lower temperature and 100 joules of work is done with external help. Then 200+ 100 = 300 joules are rejected at the higher temperature.

The coefficient of preformance

$$= \frac{H_2}{W}$$

$$= \frac{H_2}{H_1 - H_2}$$

$$= \frac{200}{300 - 200} = 2$$

Therefore the coefficient of performance of a refrigerator = 2.

In the case of a heat engine, the efficiency cannot be more than 100% but in the case of a refrigerator, the coefficient of performance can be much higher than 100%.

Example 6·8 *Find the efficiency of the Carnot's engine working between the steam point and the ice point*

$$T_1 = 273 + 100 = 373 \text{ K}$$

$$T_2 = 273 + 0 = 273 \text{ K}$$

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

$$= 1 - \frac{273}{373} = \frac{100}{373}$$

$$\%\ \text{efficiency} = \frac{100}{373} \times 100$$

$$= \mathbf{26{\cdot}81\%}$$

Example 6·9. *Find the efficiency of a Carnot's engine working between 127°C and 27°C.*

$$T_1 = 273 + 127 = 400 \text{ K}$$

$$T_2 = 273 + 27 = 300 \text{ K}$$

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

$$= 1 - \frac{300}{400} = 0{\cdot}25$$

$$\%\ \text{efficiency} = \mathbf{25\%}$$

Example 6·10. *A Carnot's engine whose temperature of the source is 400 K takes 200 calories of heat at this temperature and rejects 150 calories of heat to the sink. What is the temperature of the sink? Also calculate the efficiency of the engine.*

$$H_1 = 200 \text{ cal}\ ; \qquad H_2 = 150 \text{ cal}$$

$$T_1 = 400 \text{ K}\ ; \qquad T_2 = ?$$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$T_2 = \frac{H_2}{H_1} \times T_1$$

$$T_2 = \frac{150}{200} \times 400 = \mathbf{300\ K}$$

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

$$= 1 - \frac{300}{400} = 0{\cdot}25$$

$$\% \text{ efficiency} = \mathbf{25\%}$$

Example 6·11. *A Carnot's engine is operated between two reservoirs at temperatures of 450* K *and 350* K. *If the engine receives 1000 calories of heat from the source in each cycle, calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine and the work done by the engine in each cycle.* (*1* calorie = *4·2* joules).

$$T_1 = 450 \text{ K} ; \qquad T_2 = 350 \text{ K}$$

$$H_1 = 1000 \text{ cal} ; \qquad H_2 = ?$$

$$\frac{H_2}{H_1} = \frac{T_2}{T_1}$$

$$H_2 = H_1 \times \frac{T_2}{T_1}$$

$$= \frac{1000 \times 350}{450} = \mathbf{777{\cdot}77 \text{ cals}}$$

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

$$= 1 - \frac{350}{450} = \frac{100}{450}$$

$$= 0{\cdot}2222$$

$$\% \text{ efficiency} = \mathbf{22{\cdot}22\%}$$

Work done in each cycle

$$= H_1 - H_2$$

$$= 1000 - 777{\cdot}77$$

$$= 222{\cdot}23 \text{ cal}$$

$$= 222{\cdot}23 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{933{\cdot}33 \text{ joules}}$$

Example 6·12. *A Carnot's engine working as a refrigerator between 260* K *and 300* K *receives 500* calories *of heat from the reservoir at the lower temperature. Calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of work done in each cycle to operate the refrigerator.*

[*Delhi* (*Hons.*) *1974*]

$$H_1 = ? \qquad H_2 = 500 \text{ cal}$$

$$T_1 = 300 \text{ K} \qquad T_2 = 260 \text{ K}$$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} ;$$

$$H_1 = H_2 \cdot \frac{T_1}{T_2}$$

$$H_1 = \frac{500 \times 300}{260} = 576{\cdot}92 \text{ cal}$$

$$W = H_1 - H_2 = 76{\cdot}92 \text{ cal}$$

$$= 76{\cdot}92 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{323{\cdot}08 \text{ joules}}$$

Example 6 13. *A Carnot's refrigerator takes heat from water at 0°C and discards it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are discarded to the room ? What is the work done by the refrigerator in this process ? What is the coefficient of performance of the machine ?*

[*Delhi 1974*]

$$H_1 = ?$$

$$H_2 = 1000 \times 80 = 80{,}000 \text{ cal}$$

$$T_1 = 300 \text{ K}$$

$$T_2 = 273 \text{ K}$$

(1)

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$H_1 = \frac{H_2 T_1}{T_2}$$

$$= \frac{80{,}000 \times 300}{273}$$

$$H_1 = \mathbf{87{,}900 \text{ Cal}}$$

(2) Work done by the refrigerator

$$= W = J\,(H_1 - H_2)$$

$$W = 4{\cdot}2\,(87{,}900 - 80{,}000)$$

$$W = 4{\cdot}2 \times 7900$$

or

$$W = \mathbf{3{\cdot}183 \times 10^4 \text{ joules}}$$

(3) Coefficient of performance,

$$= \frac{H_2}{H_1 - H_2}$$

$$= \frac{80{,}000}{87{,}900 - 80{,}000}$$

$$= \frac{80{,}000}{7900}$$

$$= \mathbf{10{\cdot}13}$$

Example 6·14. *A carnot engine whose low temperature reservoir is at 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 high temperature reservoir be increased?* *(Delhi 1971)*

In the first case

$$\eta = 50\% = 0.5, \quad T_2 = 273+7 = 280 \text{ K.}$$

$$T_1 = ?$$

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

or
$$0.5 = 1 - \frac{280}{T_1}$$

or
$$T_1 = 560 \ K$$

In the second case

$$\eta' = 70\% = 0.7,$$

$$T_2 = 280 \ K,$$

$$T_1' = ?$$

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

$$0.7 = 1 - \frac{280}{T_1'}$$

or
$$T_1' = 840 \ K$$

Increase in temperature = 840—560 = **280 K**

6·28 Carnot's Theorem

The efficiency of a reversible engine does not depend on the nature of the working substance. It merely depends upon the temperature limits between which the engine works.

"All the reversible engines working between the same temperature limits have the same efficiency. No engine can be more efficient than a Carnot's reversible engine working between the same two temperatures."

Consider two reversible engines A and B, working between the temperature limits T_1 and T_2 (Fig. 6·15). A and B are coupled. Suppose A is more efficient than B. The engine A works as a heat engine and B as a refrigerator. The engine A absorbs an amount of heat H_1 from the source at a temperature T_1. It does external work W and transfers it to B. The heat rejected to the sink is H_2 at a temperature T_2. The engine B absorbs heat H_2' from the sink at temperature T_2 and W amount of work is done on the working substance. The heat given to the source at temperature T_1 is H_1'.

Suppose the engine A is more efficient than B.

Efficiency of the engine A

$$= \eta = \frac{H_1 - H_2}{H_1} = \frac{W}{H_1}$$

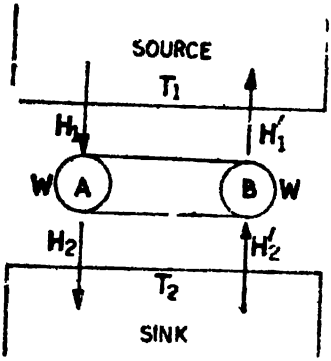


Fig. 6 16

Efficiency of the engine B

$$= \eta' = \frac{H_1' - H_2'}{H_1'} = \frac{W}{H_1'}$$

Since $\eta > \eta'$; $H_1' > H_1$

Also, $W = H_1 - H_2 = H_1' - H_2'$

$\therefore$ $H_2' > H_2$

Thus, for the two engines A and B working as a coupled system, $(H_2' - H_2)$ is the quantity of heat taken from the sink at a temperature T_2 and $(H_1' - H_1)$ is the quantity of heat given to the source at a temperature T_1. Both $(H_2' - H_2)$ and $(H_1' - H_1)$ are positive quantities. It means heat flows from the sink at a temperature T_2 (lower temperature) to the source at a temperature T_1 (higher temperature) *i.e.*, heat flows from a body at a lower temperature to a body at a higher temperature. But, no external work has been done on the system. This is contrary to the second law of thermodynamics. Thus, η cannot be greater than η'. The two engines (reversible) working between the same two temperature limits have the same efficiency. Moreover, in the case of a Carnot's engine, there is no loss of heat due to friction, conduction or radiation (irreversible processes). Thus, the Carnot's engine has the maximum efficiency. Whatever may be the nature of the working substance, the efficiency depends only upon the two temperature limits.

In a practical engine there is always loss of energy due to friction, conduction, radiation etc. and hence its efficiency is always lower than that of a Carnot's engine.

Example 6·15. *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.*

The efficiency of a Carnot's engine working between 600 K and 300 K,

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

$$= 1 - \frac{300}{600} = 0{\cdot}5$$

$$= 50\%$$

The efficiency claimed $= \eta = 52\%$

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.

6·29 Thermodynamic (or Work or Absolute) Scale of Temperature

The efficiency of a Carnot's engine does not depend upon the property of the working substance but it depends upon the temperature limits between which the engine works. The scale of temperature based on the working of the Carnot's engine is a standard scale and it does not depend upon the particular property of any substance, as in the case of other thermometric scales. Kelvin worked out the theory of the absolute scale called Kelvin's or thermodynamical scale and also showed that it agrees with the perfect gas scale.

Suppose an engine works between the temperatures θ_1 and θ_2. Here H_1 is the heat absorbed at θ_1 and H_2 is the heat rejected at θ_2

$$\eta = f(\theta_1, \theta_2)$$

$$\eta = \frac{H_1 - H_2}{H_1} = f(\theta_1, \theta_2)$$

$$\therefore \quad 1 - \frac{H_1}{H_2} = f(\theta_1, \theta_2)$$

or

$$\frac{H_1}{H_2} = \frac{1}{1 - f(\theta_1, \theta_2)} = F(\theta_1, \theta_2) \qquad \ldots(i)$$

Similarly, if the engine works between the temperature θ_2 and θ_3 and H_2 is the heat absorbed and H_3 is the heat rejected, then

$$\frac{H_2}{H_3} = F(\theta_2, \theta_3) \qquad \ldots(ii)$$

If the engine works between the temperatures θ_1 and θ_3 and H_1 is the heat absorbed and H_3 is the heat rejected, then

$$\frac{H_1}{H_3} = F(\theta_1, \theta_3) \qquad \ldots(iii)$$

From (*i*), (*ii*) and (*iii*),

$$\frac{H_1}{H_3} = \frac{H_1}{H_2} \times \frac{H_2}{H_3}$$

$$\therefore \quad F(\theta_1, \theta_3) = F(\theta_1, \theta_2) \times F(\theta_2, \theta_3)$$

$$F(\theta_1, \theta_2) = \frac{F(\theta_1, \theta_3)}{F(\theta_2, \theta_3)}$$

This temperature θ_3 is arbitrarily chosen.

This relation can be satisfied only if

$$F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

$$F(\theta_2, \theta_3) = \frac{\phi(\theta_2)}{\phi(\theta_3)}$$

and

$$F(\theta_1, \theta_3) = \frac{\phi(\theta_1)}{\phi(\theta_3)}$$

where ϕ is another function.

$$\therefore \quad \frac{H_1}{H_2} = F(\theta_1, \theta_2) = \frac{\phi(\theta_1)}{\phi(\theta_2)}$$

The expression on the right hand side represents the ratio of the two Kelvin temperatures and this can be denoted as θ_1/θ_2.

$$\therefore \quad \frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \qquad \ldots(iv)$$

The relation (*iv*) is used to represent a new scale and this does not depend upon the property of the working substance.

Efficiency

$$\eta = \frac{H_1 - H_2}{H_1} = \frac{\theta_1 - \theta_2}{\theta_1} \qquad \ldots(v)$$

$$\eta = 1 - \frac{\theta_2}{\theta_1} \qquad \ldots(vi)$$

6·30 Absolute Zero on Work Scale

Consider an engine working between the steam point and the ice point. The isothermal *AB* is at the steam point and the isothermal *OD* is at the ice point (Fig. 6·16).

$$\eta = 1 - \frac{\theta_{ice}}{\theta_{steam}}$$

$$\eta = \frac{\theta_{steam} - \theta_{ice}}{\theta_{steam}}$$

If the distance between the isothermals *AB* and *CD* is divided into 100 equal parts by drawing isothermals parallel to *AB* or *CD*, then any isothermal will be at a temperature 1° higher than the isothermal just below it. The difference in temperature between the

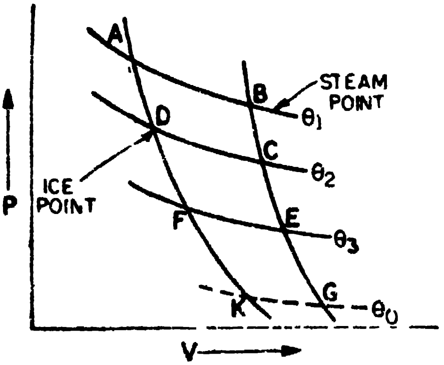


Fig. 6·16

steam point and the ice point is 100 on this scale also. In this way, the work scale (Kelvin) of temperature is fixed. Similarly, isothermals below the ice point can be drawn and an isothermal representing absolute zero can be obtained (Fig. 6·16). The isothermal *GK* represents absolute zero.

Consider an engine working between the steam point and absolute zero ($\theta_0 = 0$).

$$\eta = 1 - \frac{\theta_0}{\theta_{steam}} = 1$$

i.e., the engine has efficiency equal to 1.

Similarly an engine working between ice point and absolute zero, will have an efficiency

$$\eta' = 1 - \frac{\theta_0}{\theta_{ice}} = 1$$

But efficiency $\eta = \frac{H_1 - H_2}{H_1} = 1 - \frac{H_2}{H_1}$

If $1 - \frac{H_2}{H_1} = 1, \ \frac{H_2}{H_1} = 0$ or $H_2 = 0$

It means that if the sink is at the temperature of zero degree absolute, no heat is rejected and the whole of the available energy has been used up in doing useful work and in this case the engine will have 100% efficiency.

Thus the absolute zero temperature on the work scale is defined as the temperature at which a system undergoes a reversible isothermal process without any transfer of heat.

Absolute zero on the work scale can also be defined as that temperature of the sink at which no heat is rejected to it.

According to Kelvin-Planck statement, no engine can have 100 per cent efficiency. Thus the absolute zero temperature is not attainable.

6·31 Work Scale and Ideal Gas Scale

Consider a Carnot's reversible cycle *ABCD* (Fig. 6·17). The two isothermals are *AB* and *CD*. The temperature on the work scale is θ_1 and the ideal scale is T_1 for the isothermal *AB* and the temperature on the work scale is θ_2 and the ideal gas scale is T_2 for the isothermal *CD*. Let the pressure and volume for the points *A*, *B*, *C* and *D* be P_1, V_1 ; P_2, V_2 ; P_3, V_3 and P_4, V_4 respectively. Consider that 1 gram of an ideal gas is used as the working substance.

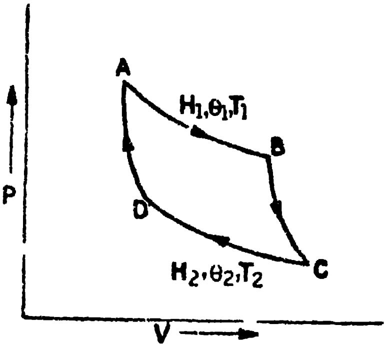


Fig 6·17

From *A* to *B*, the process is isothermal.

$$\text{Work done} = \int_{V_1}^{V_2} PdV$$

$$= rT_1 \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\therefore \quad H_1 = rT_1 \log \frac{V_2}{V_1} \quad \ldots(i)$$

Here *r* is expressed in heat units.

From *C* to *D*, the process is isothermal and a quantity of heat H_2 is rejected by the gas.

$$H_2 = -\int_{V_3}^{V_4} PdV$$

$$= -rT_2 \int_{V_3}^{V_4} \frac{dV}{V}$$

$$H_2 = rT_2 \log \frac{V_3}{V_4} \quad \ldots(ii)$$

Dividing (*i*) by (*ii*)

$$\frac{H_1}{H_2} = \frac{rT_1 \log \frac{V_2}{V_1}}{rT_2 \log \frac{V_3}{V_4}} \quad \ldots(iii)$$

Also, *A* and *B* lie on the same isothermal

$$P_1V_1 = P_2V_2$$

or
$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \qquad \text{...}(iv)$$

C and *D* lie on the same isothermal

$$P_3V_3 = P_4V_4$$

or
$$\frac{P_3}{P_4} = \frac{V_4}{V_3} \qquad \text{...}(v)$$

B and *C* lie on the same adiabatic

$$P_2V_2^{\gamma} = P_3V_3^{\gamma} \qquad \text{...}(vi)$$

A and *D* lie on the same adiabatic

$$P_1V_1^{\gamma} = P_4V_4^{\gamma} \qquad \text{...}(vii)$$

Dividing (*vi*) by (*vii*)

$$\left(\frac{P_2}{P_1}\right)\left(\frac{V_2}{V_1}\right)^{\gamma} = \left(\frac{P_3}{P_4}\right)\left(\frac{V_3}{V_4}\right)^{\gamma}$$

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

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

or
$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad \text{...}(viii)$$

Substituting this value in equation (*iii*)

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \qquad \text{...}(ix)$$

From the work scale of temperature,

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \qquad \text{...}(x)$$

$$\therefore \quad \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2} \qquad \text{...}(xi)$$

Special considerations. (*i*) If θ_1 is zero, T_1 is also zero. It means the two scales are identical at absolute zero temperature.

(*ii*) Consider that the Carnot's engine works between the steam point and the ice point and there are 100 degrees between the ice point and the steam point on the two scales.

$$\frac{\theta_{steam}}{\theta_{ice}} = \frac{T_{steam}}{T_{ice}}$$

$$\frac{\theta_{ice}+100}{\theta_{ice}} = \frac{T_{ice}+100}{T_{ice}}$$

or $$\theta_{ice} = T_{ice}$$

Therefore, the ice point is the same on the two scales.

Similarly $\theta_{steam} = T_{steam}$

Hence the two scales are completely identical.

Efficiency. The efficiency of a Carnot's engine,

$$\eta = 1 - \frac{H_2}{H_1}$$

$$= 1 - \frac{\theta_2}{\theta_1} = 1 - \frac{T_2}{T_1}$$

Let the *adiabatic expansion ratio* be ρ

$$\rho = \frac{V_3}{V_2}$$

The points *B* and *C* lie on the same adiabatic

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

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

$$= \left(\frac{1}{\rho}\right)^{\gamma-1}$$

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

6·32 Rankine Cycle

In a steam engine, water is used as the working substance. Water is converted into steam in the boiler. The steam is superheated above the boiling temperature. This superheated steam is introduced into the cylinder. For the first part, steam from the boiler enters the cylinder and moves the piston. The inlet valve remains open and the steam enters at a constant pressure. In the second part, the inlet valve closes and the steam expands adiabatically. The piston is moved through the rest of the working stroke. As soon as the piston reaches the end of *the stroke* the exhaust valve opens and the steam goes to the condenser. The steam gets condensed in the condenser.

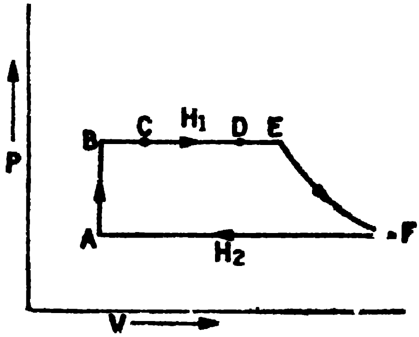


Fig. 6·18

This cycle of operations is known as the Rankine cycle, which is an ideal case. Its working is divided into the following parts :

1. *A* to *B* (Fig. 6 18) represents the compression of water and the boiler pressure is reached.

2. *B* to *C* represents the heating of water in the boiler at constant pressure and the boiling point is reached.

3. *C* to *D* represents conversion of water into steam at constant pressure.

4. *D* to *E* represents superheating of steam beyond its boiling point.

5 *E* to *F* represents the adiabatic expansion of steam in doing external work Steam is cooled and gets condensed.

6. *F* to *A* represents the rejection of steam to the condenser where the whole of the steam gets condensed. Finally, the point *A* is reached.

Efficiency. From *B* to *E*, the amount of heat absorbed is H_1 and from *F* to *A*, the amount of heat rejected is H_2.

$$\eta = 1 - \frac{H_2}{H_1}$$

6·33 Steam Engine

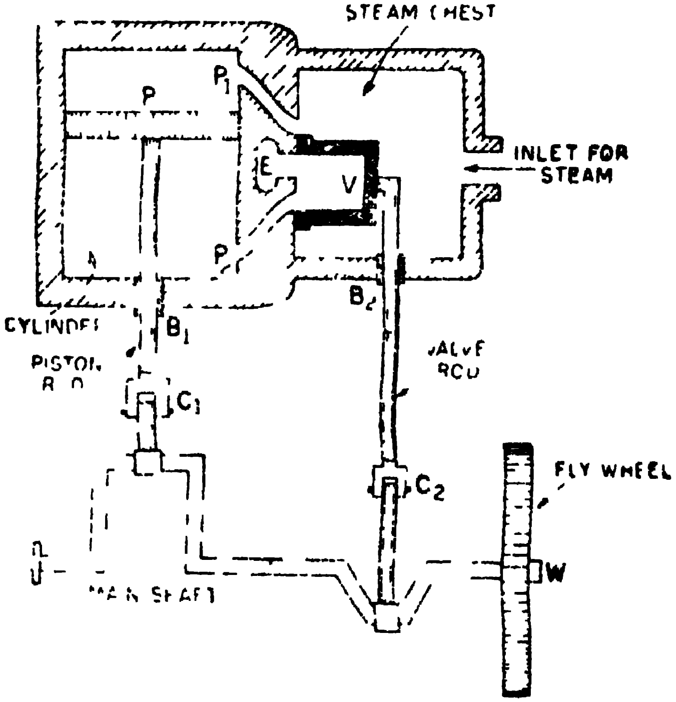


Fig. 6·19

It consists of a steam chest and a cylinder. These are connected by the steam ports P_1 and P_2. P is a piston that moves inside the cylinder. V is a sliding valve which can also move to and fro such that the port P_1 or P_2 is open to the steam chest. The piston and the sliding valve are connected to the main shaft eccentrically at diametrically opposite points such that when the shaft rotates they move in opposite directions. W is a flywheel attached to thd main shaft. The coupling between the main rod and the piston roe is such that the linear motion of the piston rod is converted to circular motion of the shaft. The machinery to be operated is connected to the main shaft.

Working 1. Steam at high pressure from the boiler enters the steam chest. The steam now is passed through the port P_1. The piston P is pushed down due to the high pressure of steam (Fig. 6.1). The sliding valve moves up. But the ports P_1 and P_2 are closed. The steam inside the cylinder expands and moves the piston further in the downward direction. At this position, the port P_1 is connected to the exhaust valve E and P_2 is opened.

2. When steam enters through the port P_2, the piston is pushed up and the sliding valve moves down.

The dead steam in the cylinder is exhausted out to the atmosphere through the exhaust valve E. Both the ports P_1 and P_2 are closed and the steam in the cylinder expands. The piston is pushed further to complete the stroke. Finally the port P_2 is closed and P_1 opens. The process is continuously repeated.

B_1 and B_2 are the stuffing boxes. These boxes allow for the free and smooth sliding of the valve rod and the piston rod. C_1 and C_2 are the cross heads. When the piston moves to and fro, the shaft is rotated and finally the machinery rotates.

Dead centres Twice in the rotation of the shaft, the force acts at right angles to the shaft. Theoretically a force does not produce any effect when it acts at right angles to the shaft. For this purpose *the flywheel* is used so that the momentum gained by the flywheel enables the shaft to rotate beyond the dead centre in each half rotation. Thus, the flywheel makes the motion of the shaft smooth and not jerky.

Power Suppose the average pressure of steam $= P$ newtons/metre^2. The length of the stroke $= L$ metres and the area of cross section of the piston $= A$ sq metres.

Total force on the piston $= (PA)$ newtons

Distance moved by the piston in a double acting steam engine

$$= 2L$$

$\therefore$ Work done for one rotation of the shaft

$$= (PA) \times 2L \text{ joules.}$$

Let the shaft rotate N times per second.

Work done per second $= (PA) \times 2L \times N$ watts

$$\text{Power of the engine} = \frac{2PLAN}{1000} \text{ kilowatts}$$

Efficiency. Most of the heat energy in the steam engine is wasted. Therefore, its efficiency is very low. It is of the order of 8 to 10%. Efficiency is the ratio of the useful mechanical work (W) done by the engine to the amount of heat (H) supplied by the fuel for the same time.

Example 6 16 *In a double acting steam engine, the average pressure of steam is 10* newtons/metre². *The length of the stroke is 1 metre and the area of the piston is 0 15 sq metre. Find the power of the engine, if it makes 5 strokes per second*

Here $P = 10^5$ newtons/metre²

$L = 1$ metre

$A = 0.15$ sq metre

$N = 5$ strokes/second

$$\text{Power} = \frac{2\,P\,L\,A\,N}{1000}$$

$$\text{Power of the engine} = \frac{2 \times 10^5 \times 1 \times 0.15 \times 5}{1000}$$

$$= 150 \text{ kilowatts}$$

6 34 Otto Cycle

In the Otto engine (internal combustion engine), air is the working substance and petrol vapour acts as the fuel. A set of ideal conditions are assumed while discussing an Otto cycle

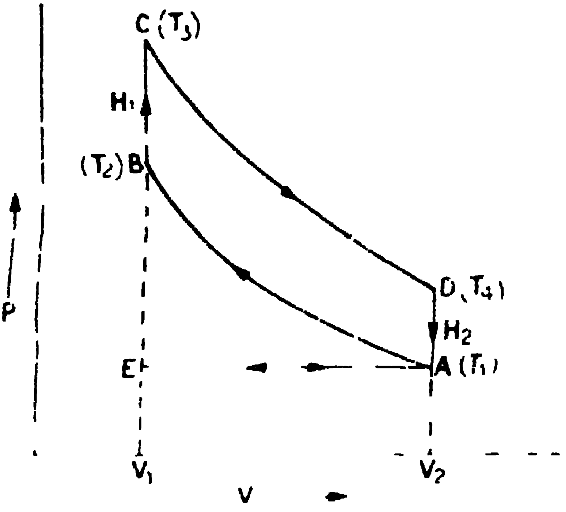


Fig. 6 20

1. The working substance is air all the time and it behaves as a perfect gas

2. There is no friction.

On the basis of these assumptions, Otto cycle can be divided into the following operations.

1. *E* to *A* (Fig. 6·20) represents the ***charging stroke***. The mixture of air and petrol vapour is allowed to enter at atmospheric pressure. The final volume is V_2 at temperature T_1.

2. *A* to *B* represents the *adiabatic compression*. There is no friction and no flow of heat through the walls of the cylinder. The volume changes from V_2 to V_1 and the temperature changes from T_1 to T_2. There is change in pressure also. This represents the *compression stroke*. The compression ratio is nearly 8 *i.e.*, $\frac{V_2}{V_1} = 8$ nearly. The pressure changes from one atmosphere to about 18 atmospheres.

3. *B* to *C* represents the *ignition stage*. A spark is produced and the mixture of air and petrol vapour is ignited. The pressure increases from 18 to about 80 atmospheres and the temperature changes from T_2 to T_3 (from 500 C to 2000 C)

4. *C* to *D* represents the *working stroke*. The gas expands adiabatically and the engine works. The volume changes from V_1 to V_2. The pressure and temperature decrease.

5. As the point *D* is reached, the exhaust valve opens. *D* to *A* represents the change of pressure to the atmospheric pressure and the temperature changes from T_4 to T_1.

6. *A* to *E* represents the *exhaust stroke*. The exhaust gases are completely discharged from the cylinder. Thus, the initial condition of the engine is restored.

Efficiency. Consider that 1 gram of the working substance is used in the process. A quantity of heat H_1 at a higher temperature is absorbed from *B* to *C*,

$$H_1 = 1 \times C_v(T_3 - T_2)$$

A quantity of heat H_2 is rejected at a lower temperature from *D* to *A*

$$H_2 = 1 \times C_v(T_4 - T_1)$$

$$\frac{H_2}{H_1} = \frac{T_4 - T_1}{T_3 - T_2} \qquad \ldots(i)$$

$$\eta = 1 - \frac{H_2}{H_1}$$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2} \qquad \ldots(ii)$$

The points *D* and *C* lie on the same adiabatic

$$\therefore \quad T_4 V_2^{\gamma - 1} = T_3 V_1^{\gamma - 1} \qquad \ldots(iii)$$

The points *A* and *B* lie on the same adiabatic

$$T_1 V_2^{\gamma - 1} = T_2 V_1^{\gamma - 1} \qquad \ldots(iv)$$

Subtracting *(iv)* from *(iii)*,

$$(T_4 - T_1) V_2^{\gamma - 1} = (T_3 - T_2) V_1^{\gamma - 1}$$

$$\frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \ldots(v)$$

Substituting this value in equation (*ii*),

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

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

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1} \quad ..(vi)$$

where ρ is the adiabatic compression ratio.

In an actual petrol engine ρ cannot be made greater than 10. If ρ is more than 10, the mixture gets ignited by itself due to compression much before the sparking takes place.

$$\eta = 1 - \left(\frac{1}{\rho}\right)^{\gamma-1}$$

If ρ = [illegible] and γ = 1.4

$$\eta = 1 - \left(\frac{1}{[illegible]}\right)^{0.4}$$

= [illegible]

If ρ = [illegible]

$$\eta = 1 - \left(\frac{1}{[illegible]}\right)^{\gamma-1}$$

= [illegible]

6.35 Internal Combustion Engine (Petrol Engine)

It consists of a cylinder and an air tight piston. It has two valves. *I* is the inlet valve and *O* is the outlet valve. These valves are opened and closed at the proper times with a suitable mechanism. The petrol vapours and air from the *carburettor* are admitted into the cylinder through the valve *I*. Here *S* acts as a sparking plug. It is also known as a four stroke engine.

1. **Charging stroke** The mixture of petrol vapours and air enters the cylinder. The piston moves down [Fig. 6.21 (*i*)]

2. **Compression stroke.** The inlet valve closes and the piston moves up. The mixture is compressed to a high pressure and the temperature rises to about 500°C [Fig. 6.21 (*ii*)]

3. **Working stroke** A spark is produced at the sparking plug and the compressed mixture of petrol and air ignites. The temperature rises to about 2000°C and a high pressure of about 15 atmospheres is developed inside the cylinder. The piston is pushed down and the shaft rotates [Fig. 6.21 (*iii*)]. Only in this stroke, work is done by the piston.

4. **Exhaust stroke.** The outlet valve opens and the burnt and unburnt gases are exhausted out into the atmosphere [Fig 6.21 (*iv*)].

The cycle repeats and the engine works.

Engine Cooling. The internal combustion engine requires cooling, although the efficiency of the engine will be higher without

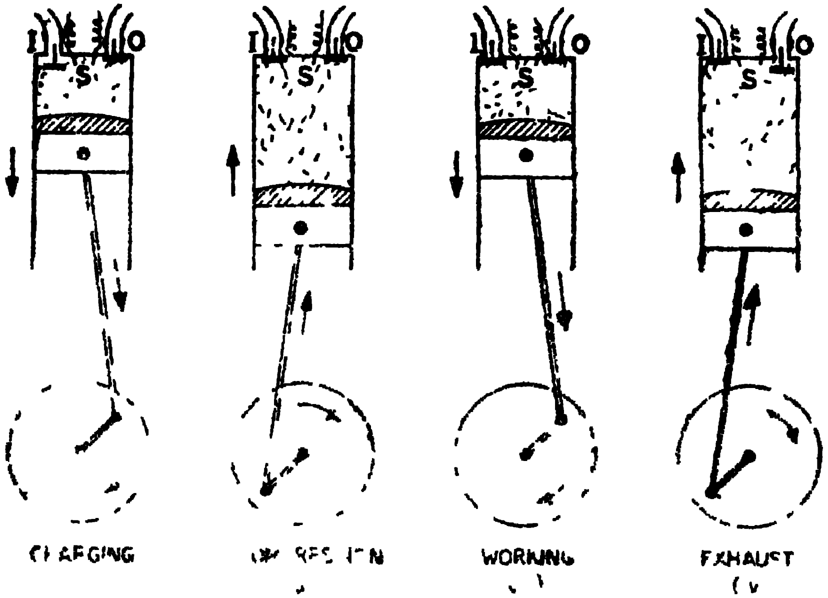


Fig. 6.21

it. The temperature of the order of 2000°C is generated inside the cylinder, although this temperature may last only for a very short interval, i.e., before expansion. If the engine is not cooled the following drawbacks will be present:

(1) Burning of the piston and exhaust valve
(2) Irregular burning of the fuel
(3) Seizure of the piston due to expansion
(4) Burning of the lubricant, and
(5) Melting of the bearing material

6.36 Diesel Engine

In the case of Diesel engine, air is admitted into the cylinder in the beginning. This air is compressed adiabatically so that the temperature is high enough to ignite the oil sprayed into the cylinder. The ideal conditions are assumed while discussing the complete cycle *viz.* (i) the working substance is air all the time and it behaves as a perfect gas and (ii) there is no friction. The cycle is called the *diesel cycle*.

1. *E* to *A* (Fig. 6.22) represents the intake of air and its volume changes to V_1. This is the *charging stroke*.

2. *A* to *B* represent the *compression stroke*. Air is compressed adiabatically. The temperature changes from T_1 to T_2 and the

volume changes from V_1 to V_2. The temperature **rises** to about 1000°C and the pressure to about 40 atmospheres.

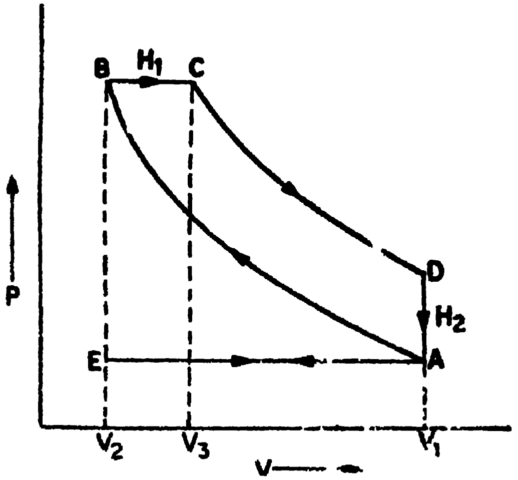


Fig. 6·22

3. B to C represents the stage when the oil is sprayed into the cylinder. The oil burns immediately. The pressure is maintained constant. The temperature changes from T_2 to T_3 (to 2000°C) and the volume changes from V_2 to V_3.

4. C to D represents the *working stroke*. The mixture of air and diesel oil vapour expand adiabatically.

5. As the point D is reached, the exhaust valve opens and the pressure drops to the point A. The volume remains constant, but temperature and pressure decrease.

6. A to E represents the *exhaust stroke*. The unburnt vapours of the oil and the mixture of gases in the cylinder are exhausted out of the cylinder.

Efficiency. From B to C, the pressure remains constant. Considering 1 gram of the working substance, the quantity of heat absorbed,

$$H_1 = 1 \times C_p(T_3 - T_2)$$

From D to A the volume remains constant.

The quantity of heat rejected,

$$H_2 = 1 \times C_v\,(T_4 - T_1)$$

$$\frac{H_2}{H_1} = \frac{C_v}{C_p} \cdot \frac{(T_4 - T_1)}{(T_3 - T_2)}$$

$$= \frac{1}{\gamma} \cdot \frac{T_4 - T_1}{T_3 - T_2}$$

$$\eta = 1 - \frac{H_2}{H_1}$$

$$= 1 - \frac{1}{\gamma}\left(\frac{T_4 - T_1}{T_3 - T_2}\right) \quad ...(1)$$

To evaluate $\left(\frac{T_4-T_1}{T_3-T_2}\right)$, all the temperatures are to be expressed in terms of T_2.

Let ρ be the adiabatic expansion ratio. Then $\rho = \frac{V_1}{V_2}$ and e the combustion expansion ratio or fuel cut off ratio $= \frac{V_3}{V_2}$.

(1) The points A and B are on the same adiabatic,

$$\therefore \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$T_1 = T_2\left[\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$= T_2\left[\frac{1}{\rho}\right]^{\gamma-1} \qquad \text{...(2)}$$

(2) The points B and C are at the same pressure

$$\therefore \quad \frac{T_3}{V_3} = \frac{T_2}{V_2}$$

or

$$T_3 = T_2\left[\frac{V_3}{V_2}\right] = T_2\,[e] \qquad \text{...(3)}$$

(3) The points C and D are on the same adiabatic.

$$\therefore \quad T_4V_4^{\gamma-1} = T_3V_3^{\gamma-1}$$

$$[\text{But } V_4 = V_1]$$

$$T_4 = T_3\left[\frac{V_3}{V_1}\right]^{\gamma-1}$$

$$= T_3\left[\frac{V_3}{V_2} \times \frac{V_2}{V_1}\right]^{\gamma-1}$$

$$T_4 = T_3\left[\frac{V_3}{V_2}\right]^{\gamma-1}\left[\frac{V_2}{V_1}\right]^{\gamma-1}$$

$$T_4 = T_3[e]^{\gamma-1}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

$$T_4 = T_2[e][e]^{\gamma-1}\left[\frac{1}{\rho}\right]^{\gamma-1}$$

$$T_4 = T_2[e]^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1} \qquad \text{...(4)}$$

$$\eta = 1 - \left[\frac{T_4-T_1}{T_3-T_2}\right]$$

$$= 1-\frac{1}{\gamma}\left[\frac{T_2[e]^{\gamma}\left[\frac{1}{\rho}\right]^{\gamma-1} - T_2\left[\frac{1}{\rho}\right]^{\gamma-1}}{T_2\,[e]-T_2}\right]$$

$$\eta = 1-\frac{1}{\gamma}\left(\frac{1}{\rho}\right)^{\gamma-1}\left[\frac{e^{\gamma}-1}{e-1}\right] \qquad \text{...(5)}$$

For the same compression ratio, the efficiency of an Otto engine is more than a diesel engine. In practice, the compression ratio for an Otto engine is from 7 to 9 and for a diesel engine it is from 15 to [illegible] Due to the higher compression ratio, an actual diesel engine has higher efficiency than the Otto (Petrol) engine. The cylinder must be strong enough to withstand very high pressure.

6.37 Multicylinder Engines

With an engine having one cylinder, the engine works only during the working stroke. The piston moves during the rest of the three strokes due to the momentum of the shaft. In a multicylinder engine, say [illegible] engine, the four cylinders are coupled. The working of each cylinder is given below :—

	First	*Second*	*Third*	*Fourth*
First quarter	Working	Exhaust	Compression	Charging
Second quarter	Exhaust	Charging	Working	Compression
Third quarter	Charging	Compression	Exhaust	Working
Fourth quarter	Compression	Working	Charging	Exhaust

In this way, the power of the engine increases and the shaft gets momentum during each quarter cycle.

6.38 Clapeyron Latent Heat Equation

Consider the isothermals *FBAE* at temperature $T + dT$ and *GCDH* at temperature T. Here *FA* and *HD* show the liquid state

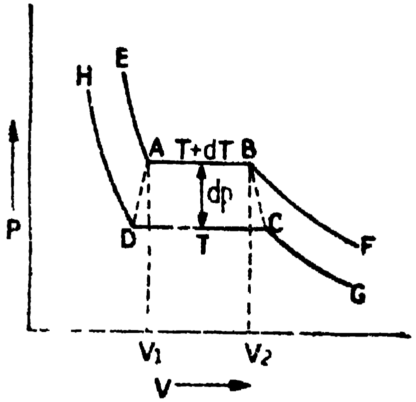


Fig. 6·23

of the substance. At *A* and *D* the substance is purely in the liquid state (Fig. 6.23). From *A* to *B* or *D* to *C* the substance is in transition from the liquid to the gaseous state and *vice versa*. At *B* and *C* the substance is purely in the gaseous state. From *B* to *F* or *C* to *G* the substance is in the gaseous state. Join *A* to *D* and *B* to *C* by dotted lines.

The cycle *ABCD* represents a complete cycle and Carnot's theorem can be applied. Suppose the volume at the point A is V_1 and temperature is $T+dT$. The pressure is just below its saturation pressure and the liquid begins to evaporate and at the point B the volume is V_2. The substance is in the vapour state. Suppose the mass of the liquid at B is one gram. The amount of heat absorbed is H_1. Here $H_1 = L+dL$, where $L+dL$ is the latent heat of the liquid at temperature $(T+dT)$.

At the point B, the pressure is decreased by dP. The vapour will expand and its temperature falls. The temperature at C is T. At this pressure and temperature T, the gas begins to condense and is converted into the liquid state. At the point D, the substance is in the liquid state. From C to D, the amount of heat rejected (given out) is H_2. Here $H_2 = L$ where L is the latent heat at temperature T. At D, increasing the pressure a little the original point A is restored. The cycle *ABCDA* is completely reversible. Applying the principle of the Carnot's reversible cycle

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$\frac{H_1 - H_2}{H_2} = \frac{T_1 - T_2}{T_2}$$

Here $$H_1 = L+dL,\ H_2 = L,$$

$$T_1 = T+dT,\ T_2 = T$$

$$H_1 - H_2 = L+dL-L = dL$$

$$T_1 - T_2 = T+dT-T = dT$$

$$\therefore \quad \frac{dL}{L} = \frac{dT}{T}$$

The area of the figure

$$ABCD = H_1 - H_2 = dL$$

$$= dP(V_2 - V_1)$$

$$\therefore \quad \frac{dP\,(V_2 - V_1)}{L} = \frac{dT}{T}$$

$$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)} \qquad \ldots(i)$$

This is called the Clapeyron's latent heat equation.

Applications. (1) *Effect of change of pressure on the melting point.*

When a solid is converted into a liquid, there is change in volume.

(*i*) If V_2 is greater than V_1

$\frac{dP}{dT}$ is a positive quantity. It means that the rate of change of pressure with respect to temperature is positive. In such cases, the melting point of the substance will increase with increase in pressure and *vice versa.*

(*ii*) If V_2 is less than V_1.

$\frac{dP}{dT}$ is a negative quantity. It means that the rate of change of pressure with respect to temperature is negative. In such cases, the melting point of the substance will decrease with increase in pressure and *vice versa.* In the case of melting ice, the volume of water formed is less than the volume of ice taken. Hence $V_2 < V_1$.

Therefore, the melting point of ice decreases with increase in pressure. Hence ice will melt at a temperature lower than zero degree centigrade at a pressure higher than the normal pressure

Ice melts at 0°C only at a pressure of 76 cm of Hg

(2) *Effect of change of pressure on the boiling point.*

When a liquid is converted into a gaseous state, the volume V_2 of the gas is always greater than the corresponding volume V_1 of the liquid *i.e.* $V_2 > V_1$.

Therefore, $\frac{dP}{dT}$ is a +ve quantity

With increase in pressure, the boiling point of a substance increases and *vice versa.* The liquid will boil at a lower temperature under reduced pressure In the case of water, the boiling point increases with increase in pressure and *vice versa.* Water boils at 100 C only at 76 cm of Hg pressure. In the laboratories, while preparing steam, the boiling point is less than 100°C because the atmospheric pressure is less than 76 cm of Hg In pressure cookers the liquid boils at a higher temperature because the pressure inside is more than the atmospheric pressure

Example 6·17. *Calculate the depression in the melting point of ice produced by one atmosphere increase of pressure. Given latent heat of ice = 80* cal per gram *and the specific volumes of 1* gram *of ice and water at 0°C are 1·091* cm³ *and 1·000* cm³ *respectively.*

(*Panjab 1963*)

Here

$$L = 80 \text{ cal} = 80 \times 4.2 \times 10^7 \text{ ergs}$$

$$T = 273 \text{ K}$$

$$dP = 1 \text{ atmosphere}$$

$$= 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$V_1 = 1{\cdot}091 \text{ cm}^3$$

$$V_2 = 1{\cdot}000 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP.T.(V_2 - V_1)}{L}$$

$$= \frac{76\times13{\cdot}6\times980\times273(1-1{\cdot}091)}{80\times4{\cdot}2\times10^7}$$

$$= \mathbf{-0{\cdot}0074\ K}$$

Therefore, the *decrease* in the melting point of ice with an increase in pressure of one atmosphere

$$= \mathbf{0{\cdot}0074\ K = 0{\cdot}0074^\circ C}$$

Example 6·18. *Find the increase in the boiling point of water at 100°C when the pressure is increased by one atmosphere. Latent heat of vaporisation of steam is 540* cal/gram *and 1* gram *of steam occupies a volume of 1677* cm³.

$$dP = 76\times13{\cdot}6\times980 \text{ dynes/cm}^2$$

$$T = 100+273$$

$$= 373 \text{ K}$$

$$L = 540\times4{\cdot}2\times10^7 \text{ ergs}$$

$$V_1 = 1{\cdot}000 \text{ cm}^3$$

$$V_2 = 1677 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dT = \frac{dP\times T(V_2-V_1)}{L}$$

$$= \frac{76\times13{\cdot}6\times980\times373\times1676}{540\times4{\cdot}2\times10^7}$$

$$= \mathbf{27{\cdot}92^\circ C}$$

Therefore, the *increase* in the boiling point of water with an increase in pressure of one atmosphere

$$= \mathbf{27{\cdot}92^\circ C}$$

$$= \mathbf{27{\cdot}92\ K}$$

Example 6·19. *Calculate the change in temperature of boiling water when the pressure is increased by 27·12* mm *of* Hg. *The normal boiling point of water at atmospheric pressure is 100°*C.

Latent heat of steam = *537* cal/g

and specific volume of steam = *1674* cm³ (*Delhi 1974*)

$$dP = 2{\cdot}712\times13{\cdot}6\times980 \text{ dynes/cm}^2$$

$$T = 100+273 = 373 \text{ K}$$

$$L = 537\times4{\cdot}2\times10^7 \text{ ergs}$$

$$V_1 = 1{\cdot}000 \text{ cm}^3$$

$$V_2 = 1674 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dT = \frac{dP \times T\,(V_2 - V_1)}{L}$$

$$= \frac{2{\cdot}712 \times 13\ 6 \times 980 \times 373 \times 1673}{537 \times 4\ 2 \times 10^7}$$

$$= 1\ \mathrm{C} \text{ or } 1\ \mathrm{K}$$

Example 6 20 *Calculate the change in the melting point of naphthalene for one atmosphere rise in pressure given that its melting point is 80°C. Latent heat of fusion is 4563* cal/mol *and increase in volume on fusion is 18 7* cm³ *per* mol *and 1* calorie $= 4\ 2 \times 10^7$ ergs

(*Delhi 1967*)

$$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)}$$

dP = 1 atmosphere

= $76 \times 13\ 6 \times 980$ dynes/cm²

dT = ?

L = 4563 cal/mol

= $4563 \times 4\ 2 \times 10^7$ ergs

$V_2 - V_1$ = 18 7 cm³/mol

T = 80+273

= 353 K

$$dT = \frac{dP\ T\,(V_2 - V_1)}{L}$$

$$= \frac{76 \times 13\ 6 \times 980 \times 353 \times 18\ 7}{4563 \times 4\ 2 \times 10^7}$$

= **0 03488 K**

Therefore the increase in the melting point of naphthalene with an increase in pressure of one atmosphere

= **0 03488 K**

= **0 03488 C**

Example 6 21 *Calculate the boiling point of benzene under a pressure of 80* cm *of mercury. The normal boiling point is 80°C. Latent heat of vaporization is 380* joules/g, *density of vapour at the boiling point is 4* g/litre *and that of the liquid 0 9* g/cm³

(*Delhi 1968*)

Here dP = 80 − 76

= 4 cm of Hg

= $4 \times 13\ 6 \times 980$ dynes/cm²

T = 80°C = 80 + 273

= 353 K

L = 380 joules/g

$$= 380 \times 10^7 \text{ ergs/g}$$

$$V_1 = \frac{1}{0{\cdot}9} = 1{\cdot}11 \text{ cm}^3$$

$$V_2 = \frac{1{,}000}{4} = 250 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T[V_2 - V_1]}$$

$$dT = \frac{dP \times T[V_2 - V_1]}{L}$$

$$dT = \frac{4 \times 13{\cdot}6 \times 980 \times 353\,[250 - 1{\cdot}11]}{380 \times 10^7}$$

$$= 1{\cdot}233 \text{ K}$$

$$= 1{\cdot}233 \text{ C}$$

The boiling point of benzene at a pressure of 80 cm of Hg

$$= 80 + 1{\cdot}233$$

$$= 81{\cdot}233 \text{ C}$$

Example 6.22 *Calculate the change in the boiling point of water when the pressure of steam on its surface is increased from 1 [illegible] to 1·10 atmospheres.*

Latent heat [illegible] of water at 100°C

= 537 cal/g

Volume of one gram of steam at 100°C

= *1,676* cm³

(*Delhi* [illegible])

$$dP = 1{\cdot}10 - 1$$

$$= 0{\cdot}10 \text{ atmosphere}$$

$$dP = 0{\cdot}10 \times 76 \times 13{\cdot}6 \times 980 \text{ dyne/cm}^2$$

$$T = 100 + 273$$

$$= 373 \text{ K}$$

$$L = 537 \text{ cals/g}$$

$$= 537 \times 4{\cdot}2 \times 10^7 \text{ ergs/g}$$

$$V_1 = 1{\cdot}00 \text{ cm}^3$$

$$V_2 = 1{,}676 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T[V_2 - V_1]}$$

$$dT = \frac{dP \times T[V_2 - V_1]}{L}$$

$$dT = \frac{0{\cdot}1 \times 76 \times 13{\cdot}6 \times 980 \times 373 \times (1{,}675)}{537 \times 4{\cdot}2 \times 10^7}$$

$$= \mathbf{2{\cdot}792\ K}$$
$$= \mathbf{2{\cdot}792^\circ C}$$

Therefore, the *increase* in the boiling point of water with an increase of 0·1 atmosphere pressure

$$= \mathbf{2{\cdot}792\ K}$$
$$= \mathbf{2{\cdot}792^\circ C}$$

Example 6·23. *Calculate the change in the melting point of ice when it is subjected to a pressure of 100 atmospheres.*

Density of ice = *0·917* g/cm^3 *and*

Latent heat of ice = *336* J/g

(*Delhi 1972*)

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dP = 100-1$$
$$= 99 \text{ atmospheres}$$
$$dP = 99\times 76\times 13{\cdot}6\times 980 \text{ dynes/cm}^2$$
$$L = 336 \text{ J/g}$$
$$= 336\times 10^7 \text{ ergs/g}$$
$$T = 273 \text{ K}$$
$$(V_2-V_1) = 1-\frac{1}{0{\cdot}917}$$
$$= -\frac{0{\cdot}083}{0{\cdot}917}$$
$$= -0{\cdot}091 \text{ cm}^3$$

$$\therefore \qquad dT = \frac{T\,dP(V_2-V_1)}{L}$$

$$dT = \frac{273\times 99\times 76\times 13{\cdot}6\times 980\times(-0{\cdot}091)}{336\times 10^7}$$
$$dT = -0{\cdot}7326 \text{ K}$$
$$= \mathbf{-0{\cdot}7326^\circ C}$$

The decrease in the melting point of ice with a pressure of 100 atmospheres

$$= \mathbf{0{\cdot}7326^\circ C}$$

Example 6·24 *Calculate the pressure required to lower melting point of ice by 1°C.*

(*L* = *79·6* cal/g, *specific volume of water at 0°C* = *1·000* cm^3 *specific volume of ice at 0°C* = *1·091* cm^3 *and 1 atmosphere pressure* = *1·013*$\times$*10*^{6} dynes/cm^2). (*Delhi 1973*)

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dT = -1 \text{ K}$$

$$T = 273 \text{ K}$$

$$V_2 - V_1 = -0{\cdot}091 \text{ cm}^3$$

$$L = 79{\cdot}6 \text{ cal/g}$$

$$= 79{\cdot}6 \times 4{\cdot}18 \times 10^7 \text{ ergs/g}$$

$$dP = \frac{L \cdot dT}{T(V_2 - V_1)}$$

$$dP = \frac{79{\cdot}6 \times 4{\cdot}18 \times 10^7 \times 1}{273 \times 0{\cdot}091} \text{ dynes/cm}^2$$

or

$$dP = \frac{79{\cdot}6 \times 4{\cdot}18 \times 10^7}{273 \times 0{\cdot}091 \times 1{\cdot}013 \times 10^6} \text{ atmospheres}$$

$$dP = 135{\cdot}2 \text{ atmospheres}$$

$\therefore$ Pressure required

$$= 135{\cdot}2 + 1$$

$$\mathbf{136{\cdot}2 \text{ atmospheres}}$$

Example 6.25. *Water boils at a temperature of 101°C at a pressure of 787* mm of Hg. *1 gram of water occupies 1,601* cm³ *on evaporation. Calculate the latent heat of steam, J = 4.2 × 10⁷* ergs/cal.
[*Delhi (Hons.) 1971*]

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 787 - 760$$

$$= 27 \text{ mm of Hg}$$

$$= 2{\cdot}7 \text{ cm of Hg}$$

$$= 2{\cdot}7 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$dT = 1°\text{C} = 1\text{K}$$

$$T = 373 \text{ K}$$

$$V_2 - V_1 = 1{,}601 - 1 = 1{,}600 \text{ cm}^3$$

$$L = ?$$

$$L = \frac{T\,dP\,(V_2 - V_1)}{dT}$$

$$L = \frac{373 \times 2{\cdot}7 \times 13{\cdot}6 \times 980 \times 1{,}600}{1} \text{ ergs/g}$$

$$L = \frac{373 \times 2{\cdot}7 \times 13{\cdot}6 \times 980 \times 1{,}600}{4{\cdot}2 \times 10^7} \text{ cal/g}$$

$$L = \mathbf{511{\cdot}3 \text{ cal/g}}$$

Example 6.26. *When lead is melted at atmospheric pressure, (the melting point is 600* K*) the density decreases from 11·01 to 10·65* g/cm³ *and the latent heat of fusion is 24.5* J/g. *What is the melting point at a pressure of 100 atmospheres?* [*Delhi (Hons.) 19[illegible]*]

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dP = 99 \text{ atmospheres}$$

$$dP = 99\times 76\times 13{\cdot}6\times 980 \text{ dynes/cm}^2$$

$$L = 24{\cdot}5 \text{ J/g}$$

$$= 24{\cdot}5\times 10^7 \text{ ergs/g}$$

$$V_1 = \frac{1}{11{\cdot}01} \text{ cm}^3$$

$$V_2 = \frac{1}{10{\cdot}65} \text{ cm}^3$$

$$V_2 - V_1 = \frac{1}{10{\cdot}65} - \frac{1}{11{\cdot}01}$$

$$= \left(\frac{0{\cdot}36}{10{\cdot}65\times 11{\cdot}01}\right) \text{cm}^3$$

$$dT = \frac{T\,dP\,(V_2-V_1)}{L}$$

$$dT = \frac{600\times 99\times 76\times 13{\cdot}6\times 980\times 0{\cdot}36}{10{\cdot}65\times 11{\cdot}01\times 24{\cdot}5\times 10^7}$$

$$dT = 0{\cdot}7539 \text{ K}$$

$$= 0{\cdot}7539 \text{ C}$$

∴ Melting point of lead at 100 atmosphere pressure

$$= 600 + 0{\cdot}7539$$

$$= 600{\cdot}7539 \text{ K}$$

Example 6.28 *Calculate under what pressure water will boil at 120°C, if the change in specific volume when 1 gram of water is converted into steam is 1,676 cm³.*

Latent heat of steam

$$= 540 \text{ cal/g}$$

$$J = 4{\cdot}2\times 10^7 \text{ ergs/cal}$$

1 atmosphere pressure

$$= 10^6 \text{ dynes/cm}^2$$

[*Delhi (Hons.) 1972*]

Here

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dT = 120-100$$

$$= 20 \text{ K}$$

$$T = 373 \text{ K}$$

$$V_2 - V_1 = 1{,}676 \text{ cm}^3$$

$$L = 540 \text{ cal/g}$$

$$= 540 \times 4{\cdot}2 \times 10^7 \text{ ergs/g}$$

$$dP = 1$$

$$dP = \frac{L.dT}{T(V_2 - V_1)}$$

$$dP = \frac{540 \times 4{\cdot}2 \times 10^7 \times 20}{373 \times 1{,}676} \text{ dynes/cm}^2$$

$$dP = \frac{540 \times 4{\cdot}2 \times 10^7 \times 20}{373 \times 1{,}676 \times 10^6} \text{ atmospheres}$$

$$dP = 0{\cdot}7254 \text{ atmosphere}$$

Pressure required $= 1 + 0{\cdot}7254$

$= \mathbf{1{\cdot}7254}$ **atmospheres**

6·39 Thermionic Emission

The electrical conductivity of metals is due to the free electrons present in the metal and not attached to any particular molecule. These free electrons continuously move within the metal and the velocity of the electrons increases with the increase in temperature of the metal. These electrons exert a pressure similar to that of a gas. However, the electrons cannot escape to the outer space because of the attractive forces at the surface that tend to keep the electrons within the metal. The attractive forces are much greater than the *electron gas pressure.* In order to escape from the surface, an electron has to do a certain amount of work called the work function (ϕ) of the surface and this is different for different metals. This energy is obtained from the kinetic energy of the electrons. At ordinary temperatures the kinetic energy of the electrons is much less than the work function and hence the electrons cannot escape from the surface. With the increase in temperature of the metal surface, the kinetic energy of the electrons increases and if the kinetic energy exceeds the work function, electrons can escape from the surface of the metal. This phenomenon is called *thermionic* emission and the electrons are called *thermo-electrons* or *thermions.* The thermionic current (I) is given by the equation

$$I = AT^2 e^{-\frac{\phi_0}{kT}}$$

where A is a constant, T is the absolute temperature of the metal, ϕ_0 is the work function of the surface at zero degree K and k is the Boltzmann's constant. I measures the thermionic current in amperes per sq cm of the emitting surface. The most commonly used emitters are (*i*) *tungsten* (*ii*) *thoriated tungsten and* (*iii*) *oxide coated cathodes containing barium or strontium.*

6·40 Richardson's Equation

Richardson derived the equation for the thermionic emission from a heated metal. He applied Clausius-Clapeyron's latent heat equation for the ejection of electrons from the surface of the metal.

Let the volume for 1 gram molecule of electrons within the metal be v_1 and outside the metal be v_2. The volume v_2 is very high as compared to v_1. The pressure of electrons under equilibrium conditions is P. The energy absorbed by N electrons during ejection from the metal surface $= W$. Here N is the Avogadro's number. Applying Clapeyron's latent heat equation

$$\frac{dP}{dT} = \frac{W}{T(v_2 - v_1)} \qquad \ldots(i)$$

As $v_2 > > v_1$, v_1 can be neglected

$$\therefore \quad \frac{dP}{dT} = \frac{W}{T v_2}$$

or

$$W \quad T v_2 \frac{dP}{dT} \qquad \ldots(ii)$$

The energy W consists of two parts. (*i*) The work function of the surface *i.e.*, energy required for ejecting N electrons just outside the metal *i.e.*, in crossing the potential barrier. This energy $= N\phi$ where ϕ is the work function of the surface.

(*ii*) The work done in admitting the ejected electrons into the electron cloud already present outside the metal. This energy is Pv_2. For one gram molecule of electrons

$$Pv_2 = R\,T = N\,k\,T$$

Here k is Boltzmann's constant

$$W = N\,\phi + N\,k\,T \qquad \ldots(iii)$$

From equations (*ii*) and (*iii*)

$$N(\phi + kT) = T\,v_2\,\frac{dP}{dT}$$

But

$$v_2 = \frac{NkT}{P}$$

$$\therefore \quad N(\phi + kT) = T\left(\frac{NkT}{P}\right) \times \frac{dP}{dT}$$

$$(\phi + kT) = \frac{kT^2}{P} \times \frac{dP}{dT}$$

$$\frac{dP}{P} = \left(\frac{\phi + kT}{kT^2}\right) dT$$

Integrating

$$\int \frac{dP}{P} = \int \frac{\phi}{kT^2}\,dT + \int \frac{dT}{T}$$

$$\log_e P = \int \frac{\phi}{kT^2}\,dT + \log_e T + \text{constant}$$

Let the constant be equal to $\log_e A_1$

$$\log_e P \quad \log_e T - \log_e A_1 = \int \frac{\phi}{kT^2}\,dT$$

$$\log_e\left(\frac{P}{A_1T}\right) = \int\frac{\phi}{kT^2}\,dT \qquad \ldots(iv)$$

Richardson suggested that ϕ also depends upon T. If ϕ_0 is the work function at 0 K, then

$$\phi = \phi_0 + \tfrac{3}{2}kT$$

$$\therefore \qquad \int\frac{\phi}{kT^2}\,dT = \int\frac{\phi_0+\frac{3}{2}kT}{kT^2}\,dT$$

$$= -\frac{\phi_0}{kT} + \tfrac{3}{2}\log_e T$$

$$= -\frac{\phi_0}{kT} + \log_e T^{\frac{3}{2}}$$

Substituting this value in equation (iv)

$$\log_e\left(\frac{P}{A_1T}\right) = -\frac{\phi_0}{kT} + \log_e T^{\frac{3}{2}}$$

$$\log_e\left(\frac{P}{A_1T^{\frac{5}{2}}}\right) = -\frac{\phi_0}{kT}$$

or

$$P = A_1\,T^{\frac{5}{2}}\,e^{-\frac{\phi_0}{kT}} \qquad \ldots(v)$$

If the number of electrons per unit volume = n then

$$P = n\,k\,T \qquad \ldots(vi)$$

Equating (v) and (vi)

$$n\,k\,T = A_1T^{\frac{5}{2}}\,e^{-\frac{\phi_0}{kT}}$$

$$n = \left(\frac{A_1}{k}\right)T^{\frac{3}{2}}\,e^{-\frac{\phi_0}{kT}} \qquad \ldots(vii)$$

Assuming the perfect gas laws to hold good in the case of an electron cloud, the mean energy of the electron,

$$\tfrac{1}{2}\,m_0\,v^2 = \tfrac{3}{2}\,kT$$

or

$$v = \left(\frac{3kT}{m_0}\right)^{\frac{1}{2}}$$

But Kundsen has shown that the number of electrons passing unit area in one second is,

$$n_0 = \frac{nv}{\sqrt{6\pi}}$$

$$\therefore \qquad n_0 = n\times\left(\frac{3kT}{6\pi m_0}\right)^{\frac{1}{2}}$$

$$= n\left(\frac{kT}{2\pi m_0}\right)^{\frac{1}{2}}$$

Substituting the value of n from equation (vii)

$$n_0 = \left[\left(\frac{A_1}{k}\right)T^{\frac{3}{2}}\;e^{-\frac{\phi_0}{kT}}\right]\left[nT^{\frac{1}{2}}\left(\frac{k}{2\pi m_0}\right)^{\frac{1}{2}}\right]$$

$$n_0 = \left[\frac{nA_1}{k}\times\left(\frac{k}{2\pi m_0}\right)^{\frac{1}{2}}\right]T^2\, e^{-\frac{\phi_0}{kT}}$$

Taking

$$\frac{nA_1}{k}\left(\frac{k}{2\pi m_0}\right)^{\frac{1}{2}} = A_2 = \text{constant}$$

$$n_0 = A_2 T^2\, e^{-\frac{\phi_0}{kT}}$$

Taking the charge on the electron e, the current density due to electron emission,

$$I = n_0 e = A_2 e T^2\, e^{-\frac{\phi_0}{kT}}$$

$$I = AT^2\, e^{-\frac{\phi_0}{kT}} \qquad \ldots(viii)$$

Here $\qquad A = (A_2 e) = \text{constant}$

Equation (*viii*) represents the Richardson's equation for thermionic emission.

The electron emitter can be heated directly or indirectly. In the case of direct heating, the current is passed through the filament which itself serves as the cathode. Tungsten and thoriated tungsten filaments are the commonly used directly heated electron emitters. The indirectly heated electron emitter consists of a heater wire surrounded by a metal sleeve in the form of a cylinder whose surface is coated with electron emitting materials. The most commonly used cathode is the indirectly heated cathode. In both the cases, filaments can be heated either by *DC* or *AC*.

The operating temperatures for tungsten thoriated tungsten and oxide coated emitters are given below.

Tungsten	2200 to 3000 K
Thoriated Tungsten	1900 K
Oxide coated cathode	1000 to 1150 K

Values of the Emission Constants

Material	ϕ_0 *in eV*	*A in* A/m^2–K	*Melting point in* K
Carbon	4.7	—	—
Nickel	5.0	2.68×10^5	1725
Platinum	5.32	3.20×10^5	2047
Tantalum	4.1	6.02×10^5	3123
Tungsten	4.52	6.02×10^5	3655

6·41. Clausius Inequality

Before considering entropy, it is necessary to establish the Clausius inequality which states that

$$\oint \frac{\delta H}{T} < 0$$

This relation is between the temperatures of an arbitrary number of heat reservoirs and the amounts of heat transferred (given up or lost).

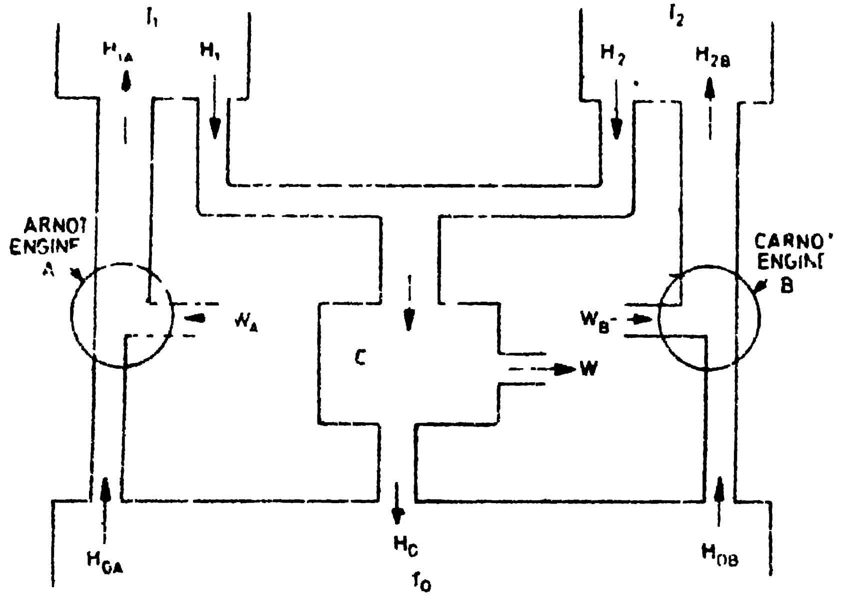


Fig. 6.24.

Consider three heat reservoirs at temperatures T_1, T_2 and T_0 (Fig 6.24)

The engine C works as a heat engine. It absorbs heat H_1 from reservoir at temperature T_1 and H_2 from reservoir at temperature T_2. The system as a whole does an amount of work W and rejects a quantity of heat H_0 to the reservoir at temperature T_0.

Carnot's engines A and B work as refrigerators. The engine A absorbs heat H_{0A} from the reservoir at temperature T_0, an amount of work W_A is supplied to it and it rejects a quantity of heat H_{1A} to the reservoir at temperature T_1. The engine B absorbs heat H_{0B} from the reservoir at temperature T_0, an amount of work W_B is supplied to it and it rejects a quantity of heat H_{2B} to the reservoir at temperature T_2.

In the general discussion given below, no restriction on the direction of interchanges of the energy is made except that the interchanges must be consistent with the first and the second laws of thermodynamics.

The engine A working as a refrigerator rejects heat H_{1A} to the reservoir at temperature T_1.

Here, $H_{1A}+H_1 = 0$ ...(*i*)

Similarly the engine B working as a refrigerator rejects heat H_{2B} to the reservoir at temperature T_2.

Here $H_{2B}+H_2 = 0$ ...(*ii*)

It means that when the three engines work simultaneously, there is no outstanding change in the temperature of reservoirs at temperatures T_1 and T_2.

Thus, there has been no change except for the reservoir at temperature T_0 and the mechanical system that supplied or absorbed work. If H_0 is not equal to the sum of H_{0A} and H_{0B}, the reservoir at temperature T_0 must have gained or lost heat. Similarly, if W is not equal to the sum of W_A and W_B, the mechanical system must have gained or lost work. According to the first law, the net flow of heat from or to a heat reservoir must necessarily be equal to the amount of work done on or by the mechanical system. As far as the first law is concerned it is a matter of indifference whether the reservoir gains or loses heat as long as the mechanical system loses or gains the same quantity of work. The consideration is different with reference to the second law.

If the heat reservoir loses heat and the mechanical system gains an equal amount of work, it means that the whole of the heat absorbed from the reservoir is converted into work but this violates the Kelvin Planck statement of the second law of thermodynamics.

Therefore, H_0 must always be greater than the sum of H_{0A} and H_{0B} except in the limiting case when they are equal.

For the engine A,

$$\frac{H_{1A}}{T_1} = \frac{H_{0A}}{T_0} \qquad \text{...}(iii)$$

For the engine B,

$$\frac{H_{2B}}{T_2} = \frac{H_{0B}}{T_0} \qquad \text{...}(iv)$$

Also the quantities, H_1 and H_2 are positive, H_0 is negative, H_{1A} and H_{2B} are negative, H_{0A} and H_{0B} are positive. Mathematically we write all the quantities as positive.

From equation (*iii*)

$$H_{0A} = \frac{T_0\,(H_{1A})}{T_1} = \frac{T_0\,(H_1)}{T_1} = T_0\left(\frac{H_1}{T_1}\right) \qquad \text{...}(v)$$

Similarly, $$H_{0B} = \frac{T_0\,(H_{2B})}{T_2} = \frac{T_0\,(H_2)}{T_2} = T_0\left(\frac{H_2}{T_2}\right) \qquad \text{...}(vi)$$

The net quantity of heat drawn from the reservoir at temperature T_0 is

$$H_0 + H_{0A}+H_{0B}$$

According to the second law, this quantity should be less than or equal to zero.

i.e.
$$H_0+H_{0A}+H_{0B} \leqslant 0$$

Substituting the values of H_{0A} and H_{0B}

$$H_0+T_0\left(\frac{H_1}{T_1}\right)+T_0\left(\frac{H_2}{T_2}\right) \leqslant 0$$

Dividing by T_0

$$\frac{H_0}{T_0}+\frac{H_1}{T_1}+\frac{H_2}{T_2} \leqslant 0 \qquad \ldots(vii)$$

In general, for a system using a large number of reservoirs, it can be written as,

$$\sum \frac{H}{T} \leqslant 0 \qquad \ldots(viii)$$

When the number of reservoirs is infinite and the heat exchanges take place by infinitesimal amounts, it can be written as

$$\int \frac{\delta H}{T} \leqslant 0 \qquad \ldots(ix)$$

Equations (*viii*) and (*ix*) represent the **Clausius inequality.** The relation holds goods for any cyclic process, reversible or irreversible.

Examples . Consider two blocks at temperatures 300 K and 200 K that are in contact. The block at higher temperature conducts heat to the block at the lower temperature. Suppose, 200 joules of heat is transferred. Here,

$$H_1 = 200 \text{ joules}; \qquad T_1 = 300 \text{ K}$$
$$H_2 = -200 \text{ joules}, \qquad T_2 = 200 \text{ K}$$

$$\therefore \quad \sum \frac{H}{T} = \frac{H_1}{T_1}+\frac{H_2}{T_2}$$
$$= \frac{200}{300}+\frac{(-200)}{200} = -\frac{1}{3}$$
$$= -0{\cdot}33 \text{ joule/degree}$$

(2) Consider an actual heat engine working between the temperatures 500 K and 300 K.

Suppose its efficiency is 20% and it takes 1000 joules of heat from the high temperature reservoir. As the efficiency is 20%.

$$\eta = 1-\frac{H_2}{H_1}$$

$$\frac{20}{100} = 1-\frac{H_2}{100}$$

or
$$H_2 = 800 \text{ joules}$$

$$\therefore \quad \sum \frac{H}{T} = \frac{H_1}{T_1}+\frac{H_2}{T_2}$$

Here $\quad H_1 = +1000$ joules

$H_2 = -800$ joules (since heat is rejected)

$T_1 = 500$ K

$T_2 = 300$ K

$$\sum \frac{H}{T} = \frac{1000}{500} + \frac{-800}{300}$$

$$= -\frac{2}{3} \text{ joule/degree}$$

(3) Consider a Carnots reversible engine working between the temperatures 500 K and 300 K. Suppose 1000 joules of heat energy is drawn from the high temperature reservoir.

Here
$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$\frac{1000}{500} = \frac{H_2}{300}$$

or
$$H_2 = 600 \text{ joules}$$

$$\sum \frac{H}{T} = \frac{H_1}{T_1} + \frac{H_2}{T_2}$$

Here $\quad H_1 = +1000$ joules

$H_2 = -600$ joules

$T_1 = 500$ K

$T_2 = 300$ K

$$\therefore \quad \sum \frac{H}{T} = \frac{1000}{500} + \frac{(-600)}{300}$$

or
$$\sum \frac{H}{T} = 0$$

This example shows $\sum \frac{H}{T} = 0$, only in the limiting case and in no case $\sum \frac{H}{T}$ is greater than zero.

6·42. Entropy and the Second Law of Thermodynamics

Consider a closed system undergoing a reversible process from state 1 to state 2 along the path A and from state 2 to state 1 along the path B (Fig. 6·25). As this is a reversible cyclic process

$$\oint \frac{\delta H}{T} = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \text{...(i)}$$

Now consider the reversible cycle from state 1 to state 2 along the path A and from state 2 to state 1 along the path C

For this reversible cyclic process

$$\int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} = 0 \qquad \ldots(ii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2C}^{1C} \frac{\delta H}{T} \qquad \ldots(iii)$$

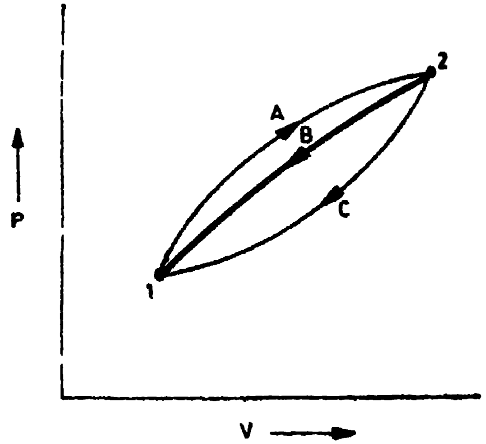


Fig 6·25

This shows that $\int \frac{\delta H}{T}$ has the same value for all the reversible paths from state 2 to state 1. The quantity $\int \frac{\delta H}{T}$ is independent of the path and is a function of the end states only, therefore it is a property.

This property is called entropy. Entropy is a thermodynamical property and is defined by the relation

$$dS = \frac{\delta H}{T} \qquad \ldots(iv)$$

or

$$S_2 - S_1 = \int_1^2 \frac{\delta H}{T} \qquad \ldots(v)$$

The quantity $S_2 - S_1$ represents the change in entropy of the system when it is changed from state 1 to state 2.

6·43 Entropy changes of a Closed System During an Irreversible Process

Consider a reversible cycle where the state is changed from 1 to 2 along the path A and 2 to 1 along the path B (Fig 6·26).

For a reversible cyclic process

$$\oint \delta H = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad ...(i)$$

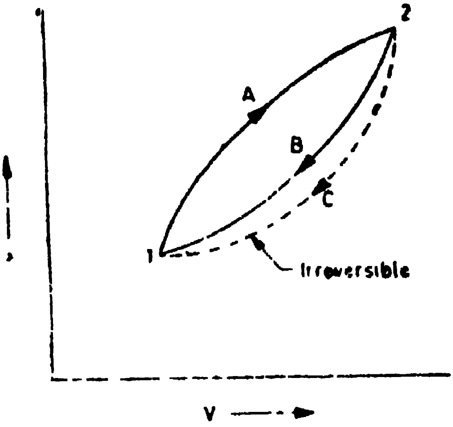


Fig. 6 26

Now consider an irreversible path C from state 2 to state 1.

Applying Clausius inequality for the cycle of processes A and C

$$\int \frac{\delta H}{T} \leqslant 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} \leqslant 0 \qquad ...(ii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} - \int_{2C}^{1C} \frac{\delta H}{T} \geqslant 0$$

Since path B is reversible and entropy is a property

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2B}^{1B} dS = \int_{2C}^{1C} dS$$

$$\therefore \qquad dS > \frac{\delta H}{T} \qquad ...(iii)$$

or

$$S_2 - S_1 > \int_1^2 \delta H \qquad ...(iv)$$

To conclude,

For a reversible process

$$S_2 - S_1 = \int_1^2 \frac{\delta H}{T}$$

and for an irreversible process

$$S_2 - S_1 > \int_1^2 \frac{\delta H}{T}$$

Equation (*iv*) shows that the effect of irreversibility is always to increase the entropy of a system.

6·44 Entropy

Consider adiabatics L and M on the $P-V$ indicator diagram (Fig. 6·27). All along the adiabatic L, with change in pressure there is change in volume and temperature. This shows that all along the adiabatics L or M, there is change of temperature. Consider the isothermals at temperatures T_1, T_2 and T_3. $ABCD$ represents the Carnot's reversible cycle. From A to B, heat energy H_1 is absorbed at temperature T_1. From C to D, heat energy H_2 is rejected at temperature T_2.

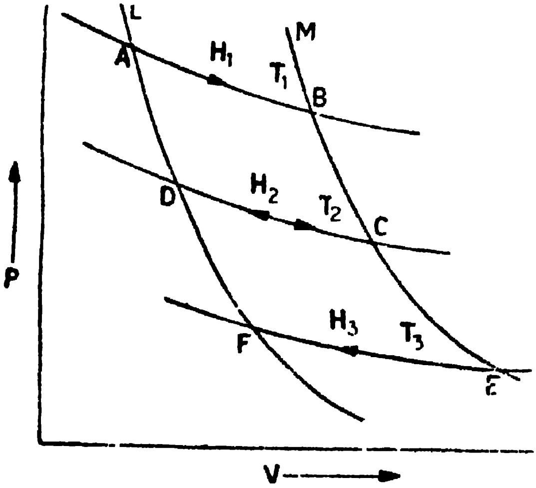


Fig. 6·27

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Similarly considering the cycle $DCEF$

$$\frac{H_2}{T_2} = \frac{H_3}{T_3}$$

$$\therefore \qquad \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_3}{T_3} = \text{constant}$$

From one adiabatic to the other adiabatic, heat energy is either absorbed or rejected. The quantity of heat absorbed or rejected is not constant but it depends upon the temperature. Higher the temperature, more is the heat energy absorbed or rejected and *vice versa*. The quantity H/T between two adiabatics is constant and this is called the change in entropy. Let the entropy for the adiabatics L and M be S_1 and S_2 respectively.

Here S_1 and S_2 are arbitrary quantities.

$$S_2 - S_1 = \frac{H}{T} \text{ constant.}$$

If the adiabatics are very close, and the heat absorbed or rejected is δH at a temperature T,

Change in entropy

$$dS = \frac{\delta H}{T} \qquad \ldots(1)$$

In general, the change in entropy

$$= \int_{S_1}^{S_2} dS = S_2 - S_1 = \int_A^B \frac{\delta H}{T} \qquad \ldots(2)$$

$\int_A^B \frac{\delta H}{T} = \int_{S_1}^{S_2} dS$ represents the thermodynamic co-ordinate of a system. This integral refers to the value of the function at the final state minus its value at the initial state. This function is called entropy and is represented by S. Moreover, dS is an exact differential since it is the differential of an actual function.

All along the adiabatic, $\delta H = 0$. Therefore, the change in entropy along an adiabatic is zero or the entropy all along the adiabatic is constant. *Thus entropy remains constant during an adiabatic reversible process. When heat is absorbed during a process there is increase in entropy and when heat is rejected during a process there is decrease in entropy.*

6·45 Change in Entropy in a Reversible Process (Carnot's Cycle

Consider a complete reversible process [Carnot's cycle] $ABCDA$ (Fig. 6·28). From A to B, heat energy H_1 is absorbed by the working substance at temperature T_1. The gain in entropy of the working substance from A to $B = H_1/T_1$. (H_1/T_1 is the decrease in entropy of the source from which the amount of heat H_1 is drawn at a temperature T_1). From B to C there is no change in entropy because BC is an adiabatic. From C to D, heat energy H_2 is rejected by the working substance at a temperature T_2. The loss in entropy of the working substance from C to $D = H_2/T_2$. (H_2/T_2 is also the gain in entropy of the sink to which the amount of heat H_2 is rejected at a temperature T_2). From D to A there is no change in entropy. Thus

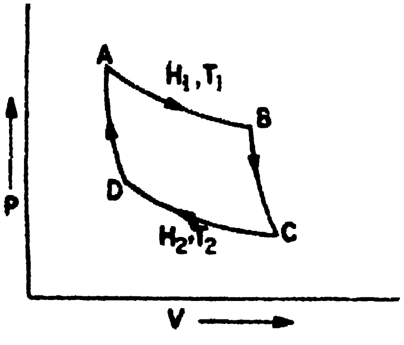


Fig. 6·28

the total gain in entropy by the working substance in the cycle $ABCDA$

$$= \frac{H_1}{T_1} \quad \frac{H_2}{T_2}$$

But for a complete reversible process

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Hence the total change in entropy of the working substance in a complete reversible process

$$= \oint dS = \frac{H_1}{T_1} - \frac{H_1}{T_2} = 0.$$

6·46 Change in Entropy in an Irreversible Process

In an irreversible process like conduction or radiation, heat is lost by a body at a higher temperature T_1 and is gained by the body at a lower temperature T_2. Here T_1 is greater than T_2.

Let the quantity of heat given out by a body at a temperature T_1 be H and the heat gained by the body at a temperature T_2 be H. Consider the hot and the cold bodies as one system.

Loss in entropy of the hot body $= -\frac{H}{T_1}$

Gain in entropy of the cold body $= \frac{H}{T_2}$

Therefore, the total increase in entropy of the system

$$= \frac{H}{T_2} - \frac{H}{T_1}.$$

It is a positive quantity because T_2 is less than T_1. Thus the entropy of the system increases in all irreversible processes.

6·47 Third Law of Thermodynamics

In all heat engines, there is always loss of heat in the form of conduction, radiation and friction. Therefore, in actual heat engines $\frac{H_1}{T_1}$ is not equal to $\frac{H_2}{T_2}$.

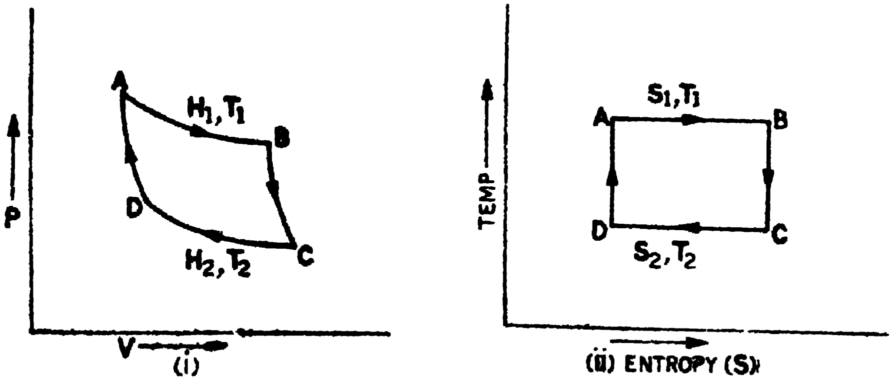
$\therefore \frac{H_1}{T_1} - \frac{H_2}{T_2}$ is not zero but it is a positive quantity. When cycle after cycle is repeated, the entropy of the system increases and tends to a maximum value. When the system has attained the maximum value, a stage of stagnancy is reached and no work can be done by the engine at this stage. In this universe the entropy is increasing and ultimately the universe will also reach a maximum value of entropy when no work will be possible. With the increase in entropy, the disorder of the molecules of a substance increases. The entropy is also a measure of the disorder of the system. With decrease in entropy, the disorder decreases. ***At absolute zero temperature, the entropy tends to zero and the molecules of a substance or a system are in perfect order (well arrenged). This is the third law of thermodynamics.***

Example. The molecules are more free to move in the gaseous state than in the liquid state. The entropy is more in the gaseous state than in the liquid state. The molecules are more free to move in the liquid state than in the solid state. The entropy is more in the liquid state than in the solid. Thus when a substance is converted from a solid to a liquid and then from the liquid to the solid state, the entropy increases and *vice versa*. When ice is converted into water and then into steam, the entropy and disorder of the molecules increase. When steam is converted into water and then into ice, the entropy and disorder of the molecules decrease. ***Hence entropy is a measure of the disorder of the molecules of the system.***

By any ideal procedure, it is impossible to bring any system to absolute zero temperature performing a finite number of operations. This is called the principle of unattainability of absolute zero. Thus according to Fowler and Guggenheim, the unattainability principle is called the third law of thermodynamics.

6·48 Temperature-Entropy Diagram

The temperature-entropy diagram is used in engineering and meteorology. Consider the Carnot's cycle $ABCDA$ [Fig. 6·29 (*i*)]. From A to B, heat energy H_1 is absorbed at temperature T_1. The increase in entropy S_1 takes place from A to B [Fig. 6·29 (*ii*)]. From B to C, there is no change in entropy. The tempetature decreases at constant entropy. From C to D, there is decrease in entropy (S_2) at constant temperature T_2. From D to A, there is no change in entropy but the temperature increases.



(i) (ii)

Fig. 6·29

The area $ABCD$ in the temperature-entropy diagram represents the actual amount of energy converted into work [Fig. 6·29 (*ii*)].

The area $\quad ABCD = S_1(T_1-T_2) = S_2(T_1-T_2)$

But $\quad S_1 = \dfrac{H_1}{T_1}$ and $S_2 = \dfrac{H_2}{T_2}$

Here $$S_1 = S_2 = \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_1-H_2}{T_1-T_2}$$

∴ Area $$ABCD = \frac{(H_1-H_2)(T_1-T_2)}{T_1-T_2} = H_1-H_2$$

Therefore, the area $ABCD$ represents the energy converted to work

Efficiency $$= \frac{H_1-H_2}{H_1} = 1-\frac{H_2}{H_1} = 1-\frac{T_2}{T_1}$$

Here H_2 is the unavailable energy.

$$H_2 = \frac{H_1}{T_1}\times T_2 = S_1\times T_2$$

The unavailable energy depends on the change in entropy at temperature T_1 and the temperature T_2.

6·49 Entropy of Perfect Gas

Consider one gram of a perfect gas at a pressure P, volume V and temperature T. Let the quantity of heat given to the gas be δH.

$$\delta H = dU+\delta W$$

$$\delta H = 1\times C_V\times dT+\frac{PdV}{J} \qquad \text{...}(i)$$

$$\delta H = TdS$$

∴ $$TdS = C_V dT+\frac{PdV}{J} \qquad \text{...}(ii)$$

Also $$PV = rT$$

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

∴ $$TdS = C_V dT+\frac{rT\,dV}{JV}$$

$$dS = C_V\frac{dT}{T}+\frac{r}{J}\frac{dV}{V}$$

Integrating, $$\int_{S_1}^{S_2} dS = C_V\int_{T_1}^{T_2}\frac{dT}{T}+\frac{r}{J}\int_{V_1}^{V_2}\frac{dV}{V}$$

$$S_2-S_1 = C_V\log_e\frac{T_2}{T_1}+\frac{r}{J}\log_e\frac{V_2}{V_1} \qquad \text{...}(iii)$$

$$S_2-S_1 = C_v\times 2{\cdot}3026\log_{10}\frac{T_2}{T_1}+\frac{r}{J}\times 2{\cdot}3026\log_{10}\frac{V_2}{V_1} \qquad \text{...}(iv)$$

The change in entropy can be calculated in terms of pressure also.

$$PV = rT$$

Differentiating

$$PdV+VdP = rdT$$

or $$PdV = rdT-VdP$$

Substituting the value of PdV in equation (*ii*)

$$TdS = C_V \times dT + \frac{rdT}{J} - \frac{VdP}{J}$$

$$TdS = \left(C_V + \frac{r}{J}\right) dT - \frac{VdP}{J}$$

But $$C_V + \frac{r}{J} = C_P$$

$$\therefore \quad dS = C_P \frac{dT}{T} - \frac{VdP}{JT}$$

Also $$PV = rT$$

or $$\frac{V}{T} = \frac{r}{P}$$

$$\therefore \quad dS = C_P \frac{dT}{T} - \frac{r}{J} \frac{dP}{P}$$

Integrating

$$\int_{S_1}^{S_2} dS = C_P \int_{T_1}^{T_2} \frac{dT}{T} - \frac{r}{J} \int_{P_1}^{P_2} \frac{dP}{P}$$

$$S_2 - S_1 = C_P \log_e \frac{T_2}{T_1} - \frac{r}{J} \log_e \frac{P_2}{P_1} \qquad \ldots(v)$$

$$S_2 - S_1 = C_P \times 2{\cdot}3026 \times \log_{10} \frac{T_2}{T_1} - \frac{r}{J} \times 2{\cdot}3026 \log_{10} \frac{P_2}{P_1} \qquad \ldots(vi)$$

Note. r is the ordinary gas constant and has to be taken in units of work, C_P represents the specific heat for 1 gram of a gas at constant pressure.

If C_P represents gram molecular specific heat of a gas at constant pressure and R the universal gas constant, then

$$S_2 - S_1 = C_P \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1} - \frac{R}{J} \times 2{\cdot}3026 \log_{10} \frac{P_2}{P_1} \qquad \ldots(vii)$$

Example 6·29. *Calculate the change in entropy when 10 grams of ice at 0°C is converted into water at the same temperature.* (*Punjab 1963, Delhi 1975*)

Heat absorbed by 10 g of ice at 0°C when it is converted into water at 0°C = 10 × 80 = 800 cal

$$\therefore \quad \delta H = 800 \text{ cal}$$

$$T = 0°\text{C} = 273 \text{ K}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{800}{273} = \mathbf{2{\cdot}93\ cal/K}$$

Example 6.30 *Calculate the change in entropy when 5 kg of water at 100°C is converted into steam at the same temperature.*

Heat absorbed by 5 kg of water at 100°C when it is converted into steam at 100°C

$$= 5000 \times 540$$

$$2700000 \text{ cal}$$

$$\therefore \qquad \delta H \qquad 2700000 \text{ cal}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{2700000}{373} \qquad \mathbf{7240\ cal/K}$$

Example 6.31 *Calculate the increase in entropy when 1 gram of ice at −10°C is converted into steam at 100°C. Specific heat of ice = 0.5, latent heat of ice = 80 cal/g, latent heat of steam = 540 cal/g.* *(Bombay 1974; Delhi 1973)*

(1) Increase in entropy when the temperature of 1 gram of ice is raised from −10°C to 0°C.

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= ms \log_e \frac{T_2}{T_1}$$

$$= ms \times 2.3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 0.5 \times 2.3026 \log_{10} \frac{273}{263}$$

$$= 0.01865 \text{ cal/K}$$

(2) Increase in entropy when 1 gram of ice at 0°C is converted into water at 0°C

$$dS = \frac{\delta H}{T}$$

$$= \frac{80}{273} = 0.293 \text{ cal/K}$$

(3) Increase in entropy when the temperature of 1 g of water is raised from 0°C to 100°C.

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 1 \times 2{\cdot}3026 \log_{10} \frac{373}{273}$$

$$= 0{\cdot}312 \text{ cal/K}$$

(4) Increase in entropy when 1 g water at 100°C is converted into steam at 100°C

$$dS = \frac{\delta H}{T}$$

$$= \frac{540}{373} = 1{\cdot}417 \text{ cal/K}$$

Total increase in entropy

$$= 0{\cdot}01865 + 0{\cdot}293 + 0{\cdot}312 + 1{\cdot}447$$

$$= \mathbf{2{\cdot}07065 \text{ cal/K}}$$

Example 6·32 *One gram molecule of a gas expands isothermally to four times its volume. Calculate the change in its entropy in terms of the gas constant.*

Work done $= \int_{V_1}^{V_2} P\,dV$

But $PV = RT$

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

$$W = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= RT \log_e \frac{V_2}{V_1}$$

Here $\dfrac{V_2}{V_1} = 4$

$$W = RT \times 2{\cdot}3026 \log_{10} (4)$$

Here, W and R are in the units of work

Gain in entropy $= \dfrac{\delta H}{T}$

$$= \frac{W}{JT} = \frac{RT \times 2{\cdot}3026 \log_{10} 4}{JT}$$

$$= 1{\cdot}387 \frac{\mathbf{R}}{\mathbf{J}} \textbf{ cal/K}$$

Example 6·33 *50 grams of water at 0°C is mixed with an equal mass of water at 83°C. Calculate the resultant increase in entropy.* *(Punjab 1963)*

(*i*) $m_1 = 50$ g ; $T_1 = 273$ K
$m_2 = 50$ g ; $T_2 = 353$ K

Let the final temperature of the mixture be T K

$$m_1 s \times (T - T_1) = m_2 s(T_2 - T)$$
$$50 \times 1 \times (T - 273) = 50 \times 1 \times (353 - T)$$
$$T = 310 \text{ K}$$

(*ii*) Change in entropy by 50 g of water when its temperature rises from 273 K to 313 K.

$$= \frac{\delta H}{T}$$
$$= ms \int_{T_1}^{T} \frac{dT}{T}$$
$$= 50 \times 1 \times \log_e \frac{313}{273}$$
$$= 50 \times 2{\cdot}3026 \times \log_{10} \frac{313}{273}$$
$$= +6{\cdot}829 \text{ cal/K}$$

Here, the +ve sign indicates gain in entropy.

(*iii*) Change in entropy by 50 g of water when its temperature falls from 353 K to 313 K

$$= \frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$
$$= 50 \times 1 \times \log_e \frac{313}{353}$$
$$= 50 \times 2{\cdot}3026 \times \log_{10} \frac{313}{353}$$
$$= -6{\cdot}023 \text{ cal/K}$$

Here, the —ve sign indicates loss in entropy.

Therefore, the total gain in entropy of the system

$$= 6{\cdot}829 - 6{\cdot}023$$
$$= \mathbf{0{\cdot}806\ cal/K}$$

Example 6·34. *Calculate the change in entropy when 50* grams *of water at 15°C is mixed with 10* grams *of water at 40°C. Specific heat of water may be assumed to be equal to 1.* (*Rajasthan 1961*)

(*i*) $m_1 = 50$ g
$T_1 = 15 + 273 = 288$ K
$m_2 = 10$ grams
$T_2 = 40 + 273 = 313$ K

Let the final temperature be T K.

$$m_1 \times s \times (T - T_1) = m_2 \times s \times (T_2 - T)$$

$$50 \times 1 \times (T - 288) = 80 \times 1 \times (313 - T)$$

$$T = 303{\cdot}4 \text{ K}$$

(*ii*) Change in entropy when the temperature of 50 g of water rises from 288 K to 303·4 K

$$\frac{\delta H}{T} = ms\int_{T_1}^{T}\frac{dT}{T}$$

$$= 50 \times 1 \times 2{\cdot}3026 \times \log_{10}\frac{303{\cdot}4}{288}$$

$$= +2{\cdot}602 \text{ cal/K.}$$

(*iii*) Change in entropy when the temperature of 80 g of water decreases from 313 K to 303·4 K

$$\frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 80 \times 1 \times 2{\cdot}3026 \times \log_{10}\frac{303{\cdot}4}{313}$$

$$= -2{\cdot}487 \text{ cal/K}$$

Therefore, the net change in the entropy of the system

$$= +2{\cdot}602 - 2{\cdot}487$$

$$= +0{\cdot}115 \text{ cal/K}$$

Hence the net increase in the entropy of the system

$$= 0{\cdot}115 \textbf{ cal/K}$$

Example 6·35. *10 g of steam at 100°C is blown into 90 grams of water at 0°C, contained in a calorimeter of water equivalent 10 grams. The whole of the steam is condensed. Calculate the increase in the entropy of the system.* [*Delhi (Hons.) 1973*]

(*i*)

$$m_1 = 10 \text{ g}$$

$$T_1 = 100^\circ\text{C} = 373 \text{ K}$$

$$m_2 = 90 + 10 = 100 \text{ g}$$

$$T_2 = 273 \text{ K}$$

Let the final temperature be T K

$$10 \times 540 + 10(373 - T) = 100(T - 273)$$

$$T = 331{\cdot}2 \text{ K}$$

(*ii*) Change in entropy when the temperature of water and calorimeter rises from 273 K to 331·2 K

$$\frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 100\int_{273}^{331\cdot2}\frac{dT}{T}$$

$$= 100 \times 2{\cdot}3026 \times \log_{10}\left(\frac{331{\cdot}2}{273}\right)$$

$$= +19{\cdot}32 \text{ cal/K}$$

(*iii*) Change in entropy when 10 grams of steam at 373 K is condensed to water at 373 K

$$= \left(\frac{\delta H}{T}\right) = -\frac{10 \times 540}{273}$$

$$= -14{\cdot}47 \text{ cal/K}$$

(—ve sign indicates decrease in entropy)

(*iv*) Change in entropy when 10 grams of water at 373 K is cooled to water at 331·2 K

$$\frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$

$$= 10 \times 2{\cdot}3026 \log_{10}\left(\frac{331{\cdot}2}{373}\right)$$

$$= -1{\cdot}188 \text{ cals/K}$$

Net change in entropy

$$= 19{\cdot}32 - 14{\cdot}47 - 1{\cdot}188$$

$$3{\cdot}662 \text{ cal/K}$$

Hence the net increase in the entropy of the system

$$3{\cdot}662 \text{ cal/K}$$

Example 6.36 *1 g of water at 20°C is converted into ice at 0°C at constant pressure. Heat capacity per 1 g of water is 4.2 J/g K and that of ice is 2.1 J/g K. Heat of fusion of ice at 0°C = 335 J/g. Calculate the total change in the entropy of the system.*

(*i*) Change in entropy when the temperature of 1 g of water at 293 K falls to 273 K

$$dS = \frac{\delta H}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= 1 \times 4{\cdot}2 \int_{293}^{273} \frac{dT}{T}$$

$$= 4{\cdot}2 \times 2{\cdot}3026 \log_{10}\left(\frac{273}{293}\right)$$

$$= -0{\cdot}2969 \text{ J/K}$$

(*ii*) Change in entropy when 1 g of water at 273 K is converted into ice at 273 K

$$dS = \frac{\delta H}{T} = \frac{-1 \times 335}{273} = -1{\cdot}227 \text{ J/K}$$

(*iii*) Change in entropy when the temperature of 1 g of ice at 273 K falls to 263 K

$$dS = \frac{\delta H}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$$

$$= 1\times2{\cdot}1\times2{\cdot}3026\ \log_{10}\left(\frac{263}{273}\right)$$

$$= -0{\cdot}07834\ \text{J/K}$$

Total change in entropy of the system

$$= -0\ 2969-1{\cdot}227-0{\cdot}07834$$

$$= -\mathbf{1{\cdot}60224\ J/K}$$

Negative sign shows that there is decrease in entropy of the system.

Example 6 37. *1* kg *of water at 273* K *is brought in contact with a heat reservoir at 373* K *(1) what is the change in entropy of water when its temperature reaches 373* K *?*

(2) What is the change in entropy of (i) the reservoir and (ii) the universe.

(1) Increase in entropy when the temperature of 1000 g of water is raised from 273 K to 373 K

$$dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$$

$$= ms\times2\ 3026\ \log_{10}\frac{T_2}{T_1}$$

$$= 1000\times1\times2{\cdot}3026\ \log_{10}\frac{373}{273}$$

$$= \mathbf{312\ cal/K}$$

(2) (*i*) Change in entropy of the reservoir,

$$dS = \frac{-\delta H}{T}$$

$$= -\frac{1000\times1\times100}{373} = -\mathbf{268{\cdot}1\ cal/K}$$

Negative sign shows decrease in entropy

(2) (*ii*) Change in entropy of the universe

$$= 312-268{\cdot}1$$

$$= \mathbf{43{\cdot}9\ cal/K}$$

Therefore, the net increase in entropy of the universe

$$= \mathbf{43{\cdot}9\ cal/K}$$

6·50 Zero Point Energy

According to Kinetic theory, the energy of a system at absolute zero should be zero. It means the molecules of the system do not possess any motion. But according to the modern concept, even at absolute zero, the molecules are not completely deprived of their motion and hence possess energy. The energy of the molecules at absolute zero temperature is called **zero point energy.**

6 51 Negative Temperatures

The specific heat of a substance decreases with increase in temperature. However, the specific heat does not tend to zero as the temperature tends to infinity. This shows that the temperature has a + ve sign only.

But recent experiments by Ramsey (1956) have shown that a part of a system *i e.*, the nucleus of a solid, can have a negative temperature This sub-system is considered isolated from the main system (*i.e.*, solid lattice). The specific heat of the sub-system tends to zero at high temperature. A small amount of heat energy tends to raise the temperature of the system to infinity. It is possible to add still more energy to the sub-system at infinity and it forces the sub-system into the negative temperature region. It has been shown by microscopic statistical analysis that there is no distinction between the temperature of $+\infty$ and $-\infty$. In thermodynamics, the parameter $1/T$ is more significant than T.

The *negative* temperatures are hotter than the positive temperatures and minus zero (-0) is the hottest temperature and plus zero $(+0)$ is the coldest temperature.

The negative temperature is not possible with the system as a whole and is only an exception to the rule that only positive temperatures exist. The negative temperatures are possible only for isolable sub-systems. For all normal purposes the temperatures are always positive.

6 52 Maxwell's Thermodynamical Relations

From the two laws of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities *viz* pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting the pair are taken as independent variables.

From the first law of thermodynamics

$$\delta H = dU + \delta W$$

$$\delta H = dU + PdV$$

or $$\delta U = \delta H - PdV$$

From the second law of thermodynamics,

$$dS = \frac{\delta H}{T}$$

or $$\delta H = TdS$$

Substituting this value of δH in the first equation

$$dU = TdS - PdV \qquad \ldots(i)$$

Considering S, U and V to be functions of two independent variables x and y [here x and y can be any two variables out of P, V, T and S],

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in equation (i)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right]$$

$$- P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy\right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y\right] dx$$

$$+\left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right] dy$$

Comparing the coefficients of dx and dy, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad \ldots(ii)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots(iii)$$

Differentiating equation (ii) with respect to y and equation (iii) with respect to x

$$\frac{\partial^2 U}{\partial y \cdot \partial x} = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y\,\partial x}$$

$$-\left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y\,\partial x}$$

and

$$\frac{\partial^2 U}{\partial x\,\partial y} = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x\,\partial y}$$

$$-\left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x\,\partial y}$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later or *vice versa* is the same

It means dU is a perfect differential

$$\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial x \partial y} \quad \text{and}$$

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x}$$

$$= \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \partial y}$$

$$- \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \partial y}$$

Simplifying,

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y$$

$$= \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x \quad \ldots(10)$$

where x and y may be any two variables out of P, V, T and S

Derivation of Relations

(1) Taking T and V as independent variables and

$$x = T$$

and $y = V$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (10)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (11)$$

But $dS = \dfrac{\partial H}{T}$

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \quad (12)$$

(2) Taking T and P as independent variables and

$$x = T$$

and $y = P$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} =$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(vii)$$

or

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \qquad ..(viii)$$

(3) Taking S and V as independent variables and

$$x = S$$

and

$$y = V$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V \qquad ...(ix)$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S - T\left(\frac{\partial P}{\partial H}\right)_V \qquad ...(x)$$

(4) Taking S and P as independent variables and

$$x = S$$

and

$$y = P$$

$$\frac{\partial S}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial S}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad ..(xi)$$

or

$$\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial H}\right)_P \qquad ...(xii)$$

(5) Taking P and V as independent variables and

$$x = P \quad \text{and} \quad y = V$$

$$\frac{\partial P}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1, \quad \frac{\partial P}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1 \qquad ...(xiii)$$

(6) Taking T and S as independent variables and

$$x = T \quad \text{and} \quad y = S$$

$$\frac{\partial T}{\partial x} = 1, \frac{\partial S}{\partial y} = 1, \frac{\partial T}{\partial y} = 0, \frac{\partial S}{\partial x} = 0$$

Substituting these values in equation (*iv*)

$$\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1 \qquad ...(xiv)$$

These are the important thermodynamical relations. While solving a particular problem, the suitable equation is used.

6·53 Helmholtz Function

Helmholtz function F, is the property of a system and is given by the equation

$$F = U - TS \qquad ...(i)$$

In practice, the primary function of heat engines and other devices is to perform mechanical work. From the first law of thermodynamics, for a system working between two equilibrium states,

$$\delta H = dU + \delta W \qquad ...(ii)$$

or

$$\delta W = \delta H - dU \qquad ...(iii)$$

It means that the energy converted into work is provided partly by the heat reservoir with which the system is in contact and which gives up a quantity of heat δH and partly by the system whose internal energy decreases by $(-dU)$.

When a system undergoes a process between two equilibrium states, how much maximum work can be done by it ? This can be derived by assuming that the system exchanges heat energy only with a single heat reservoir at a temperature T_0.

From the principle of increase of entropy, it is known that the sum of the increase in entropy of the system and that of the surroundings is equal to or greater than zero. Suppose,

Increase in entropy of the system $= dS$

Increase in entropy of the surroundings (reservoir) $= dS_0$

Heat absorbed by the system from the reservoir $= \delta H$

Temperature of the reservoir T_0

$$\therefore \quad dS + dS_0 \geqslant 0 \qquad ..(iv)$$

For a reservoir, $dS_0 = \frac{-\delta H}{T_0}$ [Since reservoir has given heat]

$$\therefore \quad dS - \frac{\delta H}{T_0} \geqslant 0$$

or

$$T_0\, dS \geqslant \delta H \qquad ...(v)$$

From equations (*iii*) and (*v*)

$$\delta W \leqslant T_0 . dS - dU \qquad ...(vi)$$

The quantities U and S are the properties of the system and T_0 is a constant. Therefore, for a finite process between state 1 to state 2, by integrating equation (*vi*),

$$W \leqslant T_0\,(S_2-S_1)-(U_2-U_1) \qquad \ldots(vii)$$

$$W \leqslant (U_1-U_2)-T_0(S_1-S_2) \qquad \ldots(viii)$$

Suppose that the initial and the final temperatures are equal and are the same as that of the heat reservoir.

$$\therefore \qquad T = T_0$$

Here T is the temperature of the system.

Equation (*viii*) can be written as,

$$\therefore \qquad W_T \leqslant (U_1-U_2)_T-T(S_1-S_2)_T \qquad \ldots(ix)$$

The Helmholtz function,

$$F = U-TS$$

Therefore for two equilibrium states 1 and 2 at the same temperature T,

$$(F_1-F_2) = (U_1-TS_1)-(U_2-TS_2)$$

$$= (U_1-U_2)-T(S_1-S_2)$$

or

$$(F_1-F_2)_T = (U_1-U_2)_T-T(S_1-S_2)_T \qquad \ldots(x)$$

From (*ix*) and (*x*)

$$W_T \leqslant (F_1-F_2)_T \qquad \ldots(xi)$$

Thus the maximum work that can be done in any process between two equilibrium states at the same temperature is equal to the decrease in the Helmholtz function of the system. Here the system exchanges heat with a single heat reservoir at the same temperature. Moreover maximum work is done when the process is reversible. If the process is irreversible, the work done is less than the maximum.

It is to be remembered that the maximum work that can be done is equal to the decrease in the Helmholtz function of a system but the energy converted into work is provided partly by the system and the remaining by the heat taken from the heat reservoir.

6·54 Thermodynamic Potential or Gibbs Function

The Gibbs function G of a system is given by,

$$G = U-TS+PV$$

Consider a system that can do other forms of work, in addition to $P.dV$ work, *e.g.*, a voltatic cell. In the case of a vo'taic cell, the electrical work is $-E.dI$. Similarly for a magnetic material, the magnetic work is $-m.dH$. In general, the work will be given by $P.dV$ plus a sum of terms each being the product of intensive variable (such as P, E or m) and the differential of an extensive variable (such as dV, dI and dH). In the case of a voltaic cell, the intensive variable is E and differential of extensive variable is dI.

Suppose, in general, in addition to PdV the intensive variable is y and differential of extensive variable is dx. The work done for any reversible process,

$$\delta W = PdV + ydx$$

$$W = \int_{V_1}^{V_2} PdV + \int_{x_1}^{x_2} ydx$$

Take $\int_{x_1}^{x_2} ydx = A$

Consider a process where the system works at constant pressure P_0 and the change in volume is $(V_2 - V_1)$

$$\therefore \quad \int_{V_1}^{V_2} PdV = P_0[V_2 - V_1]$$

$$\therefore \quad W = P_0[V_2 - V_1] + A \qquad \text{...}(i)$$

For a system that exchanges heat with a reservoir temperature

$$W \leqslant (U_1 - U_2) - T_0(S_1 - S_2) \qquad \text{...}(ii)$$

$$P_0[V_2 - V_1] + A \leqslant (U_1 - U_2) - T_0(S_1 - S_2)$$

or

$$A \leqslant (U_1 - U_2) - T_0(S_1 - S_2) + P_0[V_1 - V_2] \qquad \text{...}(iii)$$

Consider a specific process, where the initial and the final states of the system and the surroundings are at the same temperature (T_0) and pressure (P_0)

$$T_0 = T \quad \text{and} \quad P_0 = P$$

From equation *(iii)*

$$A_{P,T} \leqslant (U_1 - U_2)_{P,T} - T(S_1 - S_2)_{P,T} + P[V_1 - V_2]_{P,T} \qquad \text{...}(iv)$$

But, for the Gibbs function,

$$G = U - TS + PV \qquad \text{...}(v)$$

Therefore, for two equilibrium states at the same pressure and temperature,

$$[G_1 - G_2]_{P,T} = (U_1 - U_2)_{P,T} - T[S_1 - S_2]_{P,T} + P[V_1 - V_2]_{P,T} \text{...}(vi)$$

From equations *(iv)* and *(vi)*

$$A_{P,T} \leqslant (G_1 - G_2)_{P,T} \qquad \text{...}(vii)$$

Thus the difference between Gribbs function of a system between two equilibrium states sets the maximum limit to the work in addition to PdV work, provided the initial and the final states are at the same pressure and temperature and the system exchanges heat with a single heat reservoir. The work done will be maximum when the process is reversible. The process in this case will be isothermal – isobaric. If the process is irreversible, work done will be less than the maximum.

6·55 Enthalpy

Enthalpy in an extensive thermodynamic property and is given the symbol h. Enthalpy is given by the equation

$$h = U+PV \qquad \ldots(i)$$

Enthalpy is defined as the sum of the internal energy and the product of pressure and volume.

To study the properties of this function, assume that the system undergoes an infinitesimal process from an initial equilibrium state to a final equilibrium state.

From equation (i)

$$dh = dU+PdV+VdP \qquad \ldots(ii)$$

Also

$$\delta H = dU+PdV \qquad \ldots(iii)$$

$$\therefore \quad dh = \delta H+VdP \qquad \ldots(iv)$$

Dividing by dT

$$\frac{dh}{dT} = \frac{\delta H}{dT}+V\frac{dP}{dT} \qquad \ldots(v)$$

At constant pressure (isobaric process),

$$\left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\delta H}{dT}\right)_P$$

But $\left(\frac{\delta H}{dT}\right)_P = C_P$

$$\therefore \quad \left(\frac{\partial h}{\partial T}\right)_P = C_P \qquad \ldots(vi)$$

From equation (iv), during isobaric process, $dP = 0$

$$\therefore \quad dh = \delta H$$

or

$$h_f-h_i = H \qquad \ldots(vii)$$

Therefore change in enthalpy during an isobaric process is equal to the amount of heat transferred during the process.

In a throttling process, applying first law of thermodynamics

$$H = U_f-U_i+W$$

Here $H = 0$

and $W = P_fV_f-P_iV_i$

$$\therefore \quad 0 = U_f-U_i+P_fV_f-P_iV_i$$

or

$$U_i+P_iV_i = U_f+P_fV_f$$

or

$$h_i = h_f \qquad \ldots(viii)$$

Therefore in a throttling process, there in no change in enthalpy of the system. The initial and the final enthalpies are equal.

6.56 C_P, C_V and μ

The specific heat at constant pressure C_P, the specific heat at constant volume C_V and the Joule-Kelvin coefficient μ are defined as follows :

$$C_P = \left(\frac{\partial h}{\partial T}\right)_P \quad \ldots(i)$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \ldots(ii)$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \quad \ldots(iii)$$

These three quantities are defined in terms of the thermodynamic properties *viz* pressure, volume temperature, internal energy and enthalpy Hence, C_P, C_V and μ are also thermodynamic properties of a substance

6.57 Maxwell's Equations (Alternative Method)

The properties of pure substances can conveniently be represented in terms of the four functions : internal energy, enthalpy, Helmholtz function and Gibbs function

Internal energy U

Enthalpy $h = U + PV$

Helmholtz function

$$F = U - TS$$

Gibbs function $G = h - TS$

or $G = U - TS + PV$

All the above four quantities can be regarded as functions of P, V, T, and S

Now, consider a system undergoing an infinitesimal reversible process from one equilibrium state to another

(1) The internal energy changes by an amount

$$dU = \delta H - PdV$$

or

$$dU = TdS - PdV \quad \ldots(i)$$

Here U, T and P are supposed to be functions of S and V

(2) The enthalpy changes by an amount

$$dh = dU + PdV + VdP$$

$$dh = (TdS - PdV) + PdV + VdP$$

$$dh = TdS + VdP \quad \ldots(ii)$$

Here h, T and V are supposed to be functions of S and P

(3) The Helmholtz function changes by an amount

$$dF = dU - TdS - SdT$$

or $$dF = (TdS-PdV)-TdS-SdT$$

or $$dF = -SdT-PdV \qquad ...(iii)$$

Here F, S and P are supposed to be functions of T and V.

(4) The Gibbs function changes by an amount

$$dG = dh-TdS-SdT$$

$$dG = (TdS+VdP)-TdS-SdT$$

$$dG = -SdT+VdP \qquad ...(iv)$$

Here G, S and V are supposed to be functions of T and P.

As U, h, F and G are actual functions, their differentials are exact.

For exact differentials

$$dZ = Mdx+Ndy \qquad ...(v)$$

Here Z, M and N are all functions of x and y

$$\therefore \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \qquad ...(vi)$$

To derive the Maxwell's equations equation (vi) can be applied.

(1) From equation (i)

$$dU = TdS-PdV$$

Here $M = T$, $N = -P$, $x = S$, $y = V$

From equation (vi)

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial P}{\partial S}\right)_V \qquad ...(vii)$$

(2) From equation (ii)

$$dh = TdS+VdP$$

Here $M = T$, $N = V$, $x = S$, $y = P$

From equation (vi)

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad ...(viii)$$

(3) From equation (iii)

$$dF = -SdT-PdV$$

Here $M = -S$, $N = -P$, $x = T$, $y = V$

From equation (vi)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad ...(ix)$$

(4) From equation (iv)

$$dG = -SdT+VdP$$

Here $M = -S$, $N = V$, $x = T$, $y = P$

From equation (vi)

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(x)$$

Note. The equations for dU, dh, dF and dG can be obtained by remembering the sentence, 'Good Physicists have Studied Under Very Fine Teachers'. In this sentence, the letters, G, P, h, S, U, V, F, and T are to be used.

The diagram to be used is shown in Fig. 6·30.

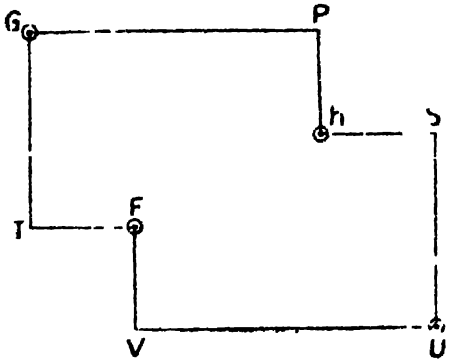


Fig. 6·30

To obtain the expression for dU, note the quantities on the two sides of U, *viz.* they are S and V. S is on the +ve direction of y-axis and V is on the −ve direction of x-axis.

$$\therefore \qquad dU = +(\quad)\,dS - (\quad)\,dV$$

The quantity associated with dS is T and with dV is P.

$$\therefore \qquad dU = TdS - PdV \qquad \ldots(i)$$

Similarly for dh

$$dh = (\quad)dS + (\quad)dP$$

$$dh = TdS + VdP \qquad \ldots(ii)$$

For dF

$$dF = -(\quad)dT - (\quad)dV$$

$$dF = -SdT - PdV \qquad \ldots(iii)$$

For dG

$$dG = -(\quad)dT + (\quad)dP$$

$$dG = -SdT + VdP \qquad \ldots(iv)$$

6·58 Joule-Kelvin Coefficient

The Joule-Kelvin effect was discussed in the chapter "Nature of heat".

The Joule-Kelvin coefficient is defined as the slope of the isenthalpic curve at any point on the temperature pressure curve.

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \qquad \ldots(i)$$

From the definition of enthalpy

$$h = U + PV \qquad \ldots(ii)$$

or
$$dh = dU+PdV+PdV \qquad ...(iii)$$

Also
$$dU = TdS-PdV$$

$\therefore$
$$dU+PdV = TdS$$

$\therefore$
$$dh = TdS+VdP \qquad ...(iv)$$

Also
$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT+\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$dh = T\left(\frac{\partial S}{\partial T}\right)_P dT+\left[T\left(\frac{\partial S}{\partial P}\right)_T+V\right]dP \qquad ...(v)$$

But
$$T\left(\frac{\partial S}{\partial T}\right)_P = C_P \qquad ...(vi)$$

The volume coefficient α is given by

$$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P$$

But
$$\left[\frac{\partial V}{\partial T}\right]_P = -\left[\frac{\partial S}{\partial P}\right]_T = \alpha V$$

$\therefore$
$$\left[\frac{\partial S}{\partial P}\right]_T = -\alpha V \qquad ...(vii)$$

Substituting these values in equation (*v*),

$$dh = C_P dT+\left[V-T\left(\frac{\partial V}{\partial T}\right)_P\right]dP \qquad ...(viii)$$

$$dT = \frac{1}{C_P}dh+\frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right]dP \qquad ...(ix)$$

But
$$dT = \left(\frac{\partial T}{\partial h}\right)_P dh+\left(\frac{\partial T}{\partial P}\right)_h dP \qquad ...(x)$$

Comparing the coefficients of equations (*ix*) and (*x*),

$$\left(\frac{\partial T}{\partial P}\right)_h = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right]$$

But
$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

$\therefore$
$$\mu = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right]$$

$$\mu C_P = \left[T\left(\frac{\partial V}{\partial T}\right)_P-V\right] \qquad ...(xi)$$

$$\mu C_P = T^2\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P \qquad ...(xii)$$

From equation (*viii*),

$$\left(\frac{\partial h}{\partial P}\right)_T = V-T\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(xiii)$$

From equations (*xi*) and (*xiii*)

$$\mu C_P = -\left(\frac{\partial h}{\partial P}\right)_T \qquad ...(xiv)$$

The Joule-Kelvin coefficient,

$$\mu = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] \qquad \ldots(xv)$$

$$\mu = \frac{V}{C_P}\left[T\left\{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P\right\} - 1\right] \qquad \ldots(xvi)$$

or

$$\mu = \frac{V}{C_P}\left[\alpha T - 1\right] \qquad \ldots(xvii)$$

For a Van der Waals gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Differentiating, keeping P constant,

$$PdV - \frac{adV}{V^2} + \frac{2ab\,dV}{V^3} = RdT$$

or

$$\frac{dV}{dT} = \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{\frac{RT}{V-b} - \frac{a}{V^2} - \frac{a}{V^2} + \frac{2ab}{V^3}}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{RV^3(V-b)}{RTV^3 - 2a(V-b)^2} \qquad \ldots(xviii)$$

Substituting this value in equation (*xvi*)

$$\mu = \frac{V}{C_P}\left[\frac{RTV^2(V-b)}{RTV^3 - 2a(V-b)^2} - 1\right]$$

$$= \frac{V}{C_P}\left[\frac{RTV^2(V-b) - RTV^3 + 2a(V-b)^2}{RTV^3 - 2a(V-b)^2}\right]$$

$$= \frac{V}{C_P}\left[\frac{2a(V-b)^2 - RTV^2 b}{RTV^3 - 2a(V-b)^2}\right] \qquad \ldots(xix)$$

From equation (*xvii*), as V and C_P are always positive, the value of μ and hence the temperature of a Van der Waals gas passing through a porous plug will depend on the value of $\alpha T - 1$.

(1) If $\alpha T > 1$, the temperature of the gas will increase.

(2) If $\alpha T < 1$, the temperature of the gas will decrease.

(3) If $\alpha T = 1$, the temperature will not change.

This temperature at which the inversion takes place is called the temperature of inversion T_i. In this case, from equation (*xvii*)

$\mu = 0$ and from equation (*xix*)

$$2a(V-b)^2 = RT_iV^2b$$

$$\therefore \qquad T_i = \frac{2a(V-b)^2}{RV^2b} \qquad \ldots(xx)$$

If $V >> b$

$$T_i = \frac{2a}{Rb} \qquad \ldots(xxi)$$

Ideal Gas. From equation (xii)

$$\mu C_P = T^2\left[\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P\right]$$

$$\therefore \qquad \mu = \frac{T^2}{C_P}\left[\frac{\partial}{\partial T}\left(\frac{V}{T}\right)_P\right]$$

For an ideal gas $\frac{V}{T} = \frac{R}{P}$

$$\mu = \frac{T^2}{C_P}\quad\frac{\partial}{\partial T}\left[\frac{R}{P}\right]_P = 0$$

Thus the Joule-Kelvin coefficient for an ideal gas is zero and the ideal gas passing through the porous gas does not show any change in temperature

6·59 Equilibrium Between Liquid and its Vapour

Applying Gibbs potential (G) it is possible to investigate the equilibrium between a liquid and its vapour or between any two phases of a substance. Consider a closed system containing a liquid in equilibrium with its saturated vapour. The temperature and pressure are equal in both the phases As each of the phases is in equilibrium, the temperature and pressure must remain constant throughout the phase and hence the thermodynamical coordinates V, S, U and G will be equal to the product of the specific value and the mass of the substance in that phase.

Suppose m_1 and m_2 are the masses in the liquid and vapour phases and g_1 and g_2 are the specific values of the Gibbs potential in the two phases. Then, for the whole system

$$G = m_1g_1+m_2g_2 \qquad \ldots(i)$$

If a small quantity of liquid changes into vapour, differentiating equation (i)

$$\delta G = \delta m_1\, g_1+\delta m_2\, g_2 \qquad \ldots(ii)$$

As the change takes place at constant temperature and pressure, the process is isothermal and isobaric

$$\therefore \qquad \delta G = 0$$

From equation (ii)

$$\delta m_1\, g_1+\delta m_2\, g_2 = 0$$

But $\delta m_1 = -\delta m_2$

$$\therefore \qquad g_1 = g_2 \qquad \ldots(iii)$$

This shows that the thermodynamical potential per unit mass will be equal in the two phases. Equation (iii) is applicable to the processes of evaporation, fusion and sublimation.

6·60 First order Phase Transitions

Consider an enclosure containing a liquid and its saturated vapour in equilibrium. If this system undergoes an isothermal, isobaric change, then

$$g_1 = g_2 \qquad ...(i)$$

Let the temperature of the system be increased from T to $T+dT$. For equilibrium

$$g_1+dg_1 = g_2+dg_2 \qquad ...(ii)$$

or

$$dg_1 = dg_2 \qquad ...(iii)$$

If the condition of saturation is satisfied,

$$\left(\frac{dg_1}{dT}\right)_{\text{sat.}} = \left(\frac{dg_2}{dT}\right)_{\text{sat.}} \qquad ...(iv)$$

The pressure also changes from P to $P+dP$,

$$\therefore \quad dg_1 = \left(\frac{\partial g_1}{\partial T}\right)_P dT + \left(\frac{\partial g_1}{\partial P}\right)_T dP \qquad ...(v)$$

or

$$\left(\frac{\partial g_1}{\partial T}\right) = \left(\frac{\partial g_1}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right) \qquad ...(vi)$$

But, for a unit mass,

$$dg = VdP - SdT \qquad ...(vii)$$

$$\therefore \quad \left(\frac{\partial g}{dP}\right)_T = V$$

and

$$\left(\frac{\partial g}{\partial T}\right)_P = -S$$

Substituting these values in equation (*vi*)

$$\left(\frac{\partial g_1}{\partial T}\right)_{\text{sat.}} = -S_1 + V_1\left(\frac{\partial P}{\partial T}\right)_{\text{sat.}}$$

Similarly,

$$\left(\frac{\partial g_2}{\partial T}\right)_{\text{sat.}} = -S_2 + V_2\left(\frac{\partial P}{\partial T}\right)_{\text{sat.}}$$

Substituting these values is equation (*iv*)

$$-S_1+V_1\left(\frac{dP}{dT}\right) = -S_2+V_2\left(\frac{dP}{dT}\right)$$

or

$$\left(\frac{dP}{dT}\right)_{\text{sat.}} = \left(\frac{S_2-S_1}{V_2-V_1}\right) \qquad ...(viii)$$

But

$$S_2-S_1 = \frac{\delta H}{T} = \frac{L}{T}$$

Here L is latent heat of vaporization

$$\therefore \quad \left(\frac{dP}{dT}\right) = \frac{L}{T(V_2-V_1)} \qquad ...(ix)$$

This is Clausius-Clapeyron latent heat equation.

This equation holds good in the first order phase transitions. In these processes there is transference of heat and hence there is change in entropy and volume. Therefore a first order phase transition can be defined as that one in which the Gibbs function with respect to pressure and temperature change discontinuously at the transition point. However, the value of the Gibbs function is the same in both the phases at equilibrium. These changes are represented graphically in Fig. 6·31.

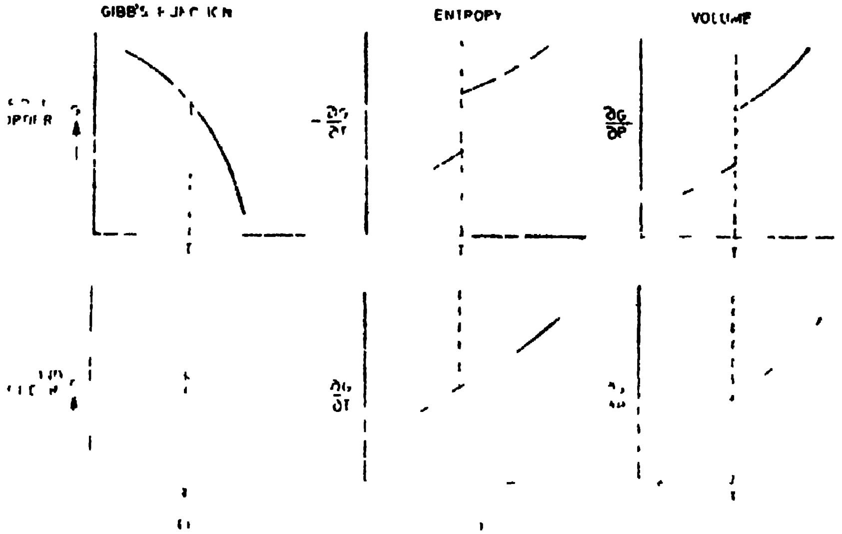


Fig. 6·31

6·61 Second Order Phase Transitions

Some recent investigations have revealed that during phase change there is no transference of heat and there is no change of volume. It has been found in the case of transition from liquid helium I to liquid helium II, that there is no transfer of heat and no change in volume. Such transitions are called second order phase transitions Second order phase transitions can be defined as the phenomenon that takes place with no change in entropy and volume at constant temperature and pressure. The examples of second order phase transitions are :

(1) Transition of liquid helium I to liquid helium II.

(2) Transition of a ferromagnetic material to a paramagnetic material at the Curie point

(3) Transition of a superconducting metal into an ordinary conductor in the absence of a magnetic field.

(4) Order-disorder transitions in chemical compounds and alloys.

In the case of second-order phase transitions there is no discontinuity of $\left(\frac{\partial G}{\partial T}\right)_P$ and $\left(\frac{\partial G}{\partial P}\right)_T$ [Fig. 6·31]. However, the second order derivatives change discontinuously.

For a phase transition,

$$g_1 = g_2$$

or
$$g_2 - g_1 = 0 \qquad \text{...(i)}$$

$$-\left(\frac{\partial g_2}{\partial T}\right)_P + \left(\frac{\partial g_1}{\partial T}\right)_P = S_2 - S_1 = 0 \qquad \text{...(ii)}$$

$$\left(\frac{\partial g_2}{\partial P}\right)_T - \left(\frac{\partial g_1}{\partial P}\right)_T = V_2 - V_1 = 0 \qquad \text{...(iii)}$$

Also

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\left(\frac{C_P}{T}\right) = \left(\frac{\partial S}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[-\left(\frac{\partial g}{\partial T}\right)_P\right]_P = -\left(\frac{\partial^2 g}{\partial T^2}\right)_P \qquad \text{...(iv)}$$

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$KV = -\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\partial}{\partial P}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_T$$

or
$$KV = -\left(\frac{\partial^2 g}{\partial P^2}\right)_T \qquad \text{...(v)}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\alpha V = \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T}\left[\left(\frac{\partial g}{\partial P}\right)_T\right]_P$$

or
$$\alpha V = \left(\frac{\partial^2 g}{\partial T \partial P}\right) \qquad \text{...(vi)}$$

Here K is the isothermal compressibility and α is the volume coefficient of expansion

From equation (*iv*)

$$\frac{C_{P_1}}{T} = -\left(\frac{\partial^2 g_1}{\partial T^2}\right)_P \qquad \text{...(vii)}$$

and
$$\frac{C_{P_2}}{T} = -\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P \qquad \text{...(viii)}$$

Subtracting (*viii*) from (*vii*)

$$\left(\frac{\partial^2 g_2}{\partial T^2}\right)_P - \left(\frac{\partial^2 g_1}{\partial T^2}\right)_P = \frac{C_{P_1} - C_{P_2}}{T} \qquad \text{...(ix)}$$

Similarly from equations (*v*) and (*vi*)

$$\left(\frac{\partial^2 g_2}{\partial P^2}\right)_T - \left(\frac{\partial^2 g_1}{\partial P^2}\right)_T = V(K_1 - K_2) \qquad \text{...(x)}$$

and $$\left(\frac{\partial^2 g_2}{\partial T.\partial P}\right)-\left(\frac{\partial^2 g_1}{\partial T.\partial P}\right) = V(\alpha_2-\alpha_1) \qquad ...(xi)$$

For second order phase transitions, there is no change in entropy and volume.

$\therefore$ $S_1 = S_2$ (at constant temperature T and pressure P)

$\therefore$ $S_1+dS_1 = S_2+dS_2$ (at temp. $T+dT$ and pressure $P+dP$)

$$\therefore \quad dS_1 = dS_2 \qquad ...(xii)$$

But $$dS = \left(\frac{\partial S}{\partial T}\right)_P dT+\left(\frac{\partial S}{\partial P}\right)_T dP$$

or $$dS = \left(\frac{C_P}{T}\right)dT-\left(\frac{dV}{dT}\right)_P dP$$

$$dS = \left(\frac{C_P}{T}\right)dT-V\alpha\, dP$$

$$\therefore \quad dS_1 = \left(\frac{C_{P1}}{T}\right)dT-V\alpha_1\, dP$$

and $$dS_2 = \left(\frac{C_{P2}}{T}\right)dT-V\alpha_2\, dP$$

$$\therefore \quad \left(\frac{C_{P1}}{T}\right)dT-V\alpha_1\, dP = \left(\frac{C_{P2}}{T}\right)dT-V\alpha_2 dP$$

$$\therefore \quad \frac{dP}{dT} = \frac{C_{P2}-C_{P1}}{TV(\alpha_2-\alpha_1)} \qquad ...(xiii)$$

Similarly by assuming $V_1 = V_2$ for second order phase transition,

$V_1 = V_2$ (at temp. T and pressure P)

$V_1+dV_1 = V_2+dV_2$ (at temp. $T+dT$ and pressure $P+dP$)

$$\therefore \quad dV_1 = dV_2$$

But $$dV = \left(\frac{\partial V}{\partial T}\right)_P dT+\left(\frac{\partial V}{\partial P}\right)_T dP$$

$$dV = V\alpha dT-VKdP$$

$$\therefore \quad dV_1 = V\alpha_1 dT-VK_1 dP$$

and $$dV_2 = V\alpha_2 dT-VK_2 dP$$

$$\therefore \quad V\alpha_1 dT-VK_1 dP = V\alpha_2 dT-VK_2 dP$$

$$\therefore \quad \frac{dP}{dT} = \left(\frac{\alpha_2-\alpha_1}{K_2-K_1}\right) \qquad ...(xiii)$$

Equations (*xii*) and (*xiii*) are called **Ehrenfest's Equations.**

Table

Maxwell's Thermodynamical Relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(i)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(ii)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \ldots(iii)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \ldots(iv)$$

Note. The first four Maxwell's thermodynamical relations need not be memorised. These can be easily written by remembering the word SP or $T_i V_e$ (sportive). In this $SPTV$ represent entropy, pressure, temperature and volume. In derving the first two relations, ∂S is written in the numerator on the left hand side of the equation and the rest of the quantities ∂P, ∂T and ∂V are written (i) in the clock-wise order and (ii) in the anticlockwise order. In the clockwise direction, the right hand side expression is with a + sign and for the anticlockwise direction, it is –ve. These equations are

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(i)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(ii)$$

Similarly to write the other equations, ∂S is written in the denominator of the right hand side of the equation and the other quantities are written (i) in the anticlockwise direction and (ii) in the clockwise direction. These equations are

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \qquad \ldots(iii)$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \qquad \ldots(iv)$$

6·62 The T dS Equations

(1) The entropy S of a pure substance can be taken as a function of temperature and volume.

$$\therefore \qquad dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad \ldots(i)$$

Multiplying both sides by T

$$T.dS = T\left(\frac{\partial S}{\partial T}\right)_V dV + T\left(\frac{\partial S}{\partial V}\right)_T dV \qquad \ldots(ii)$$

$\therefore$ But $\qquad C_V = T\left(\frac{\partial S}{\partial T}\right)_V$

and from Maxwell's relations

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Substituting these values in equation (*ii*)

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \text{...}(iii)$$

Equation (*iii*) is called the first $T\,dS$ equation.

(2) The entropy S of a pure substance can also be regarded as a function of temperature and pressure

$$\therefore \qquad dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad \text{...}(iv)$$

Multiplying both sides by T

$$T\,.\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad \text{...}(v)$$

But $\qquad C_P = T\left(\dfrac{\partial S}{\partial T}\right)_P$

and from Maxwell's relations

$$\left(\frac{dS}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Substituting these values in equation (*v*)

$$T\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP \qquad \text{...}(vi)$$

Equation (*vi*) is called the second $T\,dS$ equation.

Example 6·38. *Deduce Clapeyron's latent heat equation from Maxwell's thermodynamical relations.*

From Article 6·52, equation (*vi*)

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \text{..}(i)$$

Here $\left(\dfrac{\partial H}{\partial V}\right)_T$ represents the quantity of heat absorbed per unit increase in volume at constant temperature. This quantity of heat absorbed at constant temperature is the latent heat. If ∂H is the latent heat (L), when a unit mass of the substance changes in volume for V_1 to V_2 at constant temperature, then

$$\partial H = L \qquad \text{and} \qquad \partial V = V_2 - V_1$$

Substituting these values in equation (*i*)

$$\therefore \qquad \left(\frac{L}{V_2 - V_1}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

or

$$\frac{L}{V_2 - V_1} = T\,\frac{dP}{dT}$$

or

$$\frac{dP}{dT} = \frac{L}{T\,(V_2 - V_1)} \qquad \text{...}(ii)$$

This is Clapeyron's latent heat equation.

Example 6·39. *Show that for a homogeneous fluid*

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

Also show that for a perfect gas $C_P - C_V = R$ *and for a gas obeying Van der Waals equation*

$$C_P - C_V = R\left(1+\frac{2a}{RTV}\right)$$

Here,

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

and

$$C_V = \left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Considering S as a function of temperature and volume

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

But from equation (v) [§6·52], $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(i)$$

For a Perfect Gas

$$PV = RT$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

But,

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right)$$

$$C_P - C_V = \frac{TR^2}{PV} = \frac{R^2T}{RT} = R$$

Hence $$C_P - C_V = R \qquad \text{...(ii)}$$

[R is in heat units]

For a gas obeying Van der Waals equation

$$\left(P+\frac{a}{V^2}\right)(V-b) = RT$$

$$\left(P+\frac{a}{V^2}\right) = \frac{RT}{(V-b)}$$

$$\therefore \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

and $$\left(\frac{-2a}{V^3}+\frac{RT}{(V-b)^2}\right)\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b}$$

But $$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = \frac{T\left(\frac{R}{V-b}\right)\left(\frac{R}{V-b}\right)}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]}$$

$$C_P - C_V = \frac{RT\,(V-b)^2}{RT\,(V-b)^2}\left[\frac{R}{1-\frac{2a\,(V-b)}{V^3\,RT}}\right]$$

Neglecting b as compared to V,

$$C_P - C_V = \frac{R}{\left(1-\frac{2a}{VRT}\right)}$$

Since a is also small as compared to V

$$C_P - C_V = R\left(1+\frac{2a}{VRT}\right) \qquad \text{...(iii)}$$

[R is in heat units.]

Example 6·40. *Derive the specific heat relation or show that*

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$$

and $$C_P - C_V = -TE\alpha^2 V$$

where T is the absolute temperature, E the bulk modulus of elasticity, α the coefficient of volume expansion and V the specific volume,

$$C_P = \left(\frac{\partial H}{\partial T}\right) = T\left(\frac{\partial S}{\partial T}\right)_P$$

and $$C_V = \left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Considering S as a function of temperature and volume,

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right) + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

But from equation (v) of article 6·52,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P = C_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(i)$$

Taking the general equation of state for a gas as

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

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

$$\frac{dP}{dT} = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

At constant pressure,

$$dP = 0$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Substituting this value in equation (i)

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2 \qquad \ldots(ii)$$

$$C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \qquad \ldots(iii)$$

But $$E = V\left(\frac{\partial P}{\partial V}\right)_T$$

and $$\alpha = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_P$$

Substituting these values in equation (ii)

$$C_P - C_V = -TE\alpha^2 V \qquad \ldots(iv)$$

Example 6·41. *Show that*

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

where C_1 and C_2 represent the specific heat of a liquid and its saturated vapour and L is the latent heat of the vapour.

For a change of state from liquid to vapour,

$$S_2 - S_1 = \frac{L}{T} \quad ..(i)$$

Here S_1 and S_2 are the entropies in the liquid and vapour states respectively.

Differentiating equation (*i*) with respect to T

$$\frac{dS_2}{dT} - \frac{dS_1}{dT} = -L.\frac{1}{T^2} + \frac{1}{T} \cdot \frac{dL}{dT}$$

$$T\left(\frac{dS_2}{dT}\right) - T\left(\frac{dS_1}{dT}\right) = -\frac{L}{T} + \frac{dL}{dT}$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T} \quad ..(ii)$$

This equation is known as Clausius latent heat equation.

Example 6.42. *Calculate under what pressure water would boil at 150*°C *if the change in specific volume when 1 gram of water is converted into steam is 1676* cc. *Given latent heat of vaporization of steam = 540* cal *per gram* ; $J = 4{\cdot}2\times10^7$ ergs/cal *and one atmosphere pressure* $=10^6$ dynes/cm^2.

Here $\delta H = 540$ cal $= 540\times4{\cdot}2\times10^7$ ergs

$\partial V = 1676$ cc

$T = 373$ K, and 150°C = 423 K

$\partial T = 423-373 = 50$ K

$\partial P = ?$

Applying these values in the Maxwell's thermodynamical relation

$$\left(\frac{\delta H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{540\times4{\cdot}2\times10^7}{1676} = 373\left(\frac{\partial P}{50}\right)$$

$$\partial P = \frac{540\times4{\cdot}2\times10^7\times50}{373\times1676}$$

$$= 1{\cdot}814\times10^6 \text{ dynes/cm}^2$$

$$= 1{\cdot}814 \text{ atmospheres}$$

Therefore, the pressure at which water would boil at 150°C

$= 1{\cdot}814+1{\cdot}000$

$=$ **2·814 atmospheres**

Example 6.43. *Calculate under what pressure ice would freeze at −1*°C, *if the change in specific volume when 1 gram of water freezes into ice is 0·091* cc.

Given latent heat of fusion of ice = 80 cal/g, $J = 4{\cdot}2\times10^7$ ergs/cal *and one atmosphere pressure* $= 10^6$ dynes/cm^2.

Here,
$$\delta H = 80 \text{ cal} = 80 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$
$$\partial V = 0{\cdot}091 \text{ cc}$$
$$T = 273 \text{ K}$$
$$\partial T = 273-272 = 1 \text{ K}$$
$$\partial P = ?$$

Applying these values in the Maxwell's thermodynamical relation,

$$\left(\frac{\delta H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$
$$\frac{80 \times 4{\cdot}2 \times 10^7}{0{\cdot}091} = \frac{273 \times \partial P}{1}$$
$$\partial P = 135{\cdot}2 \times 10^6 \text{ dynes/cm}^2$$
$$= 135{\cdot}2 \text{ atmospheres}$$

Therefore, the pressure under which ice would freeze = atmospheric pressure + $\partial P = 1 + 135{\cdot}2 =$ **136·2 atmospheres**

Example 6·44. *Calculate the specific heat of saturated steam given that the specific heat of water at 100°C = 1·01 and latent heat of vaporization decreases with rise in temperature at the rate of 0·64 cal K. Latent heat of vaporization of steam = 540* cal

$$C_1 = 1{\cdot}01 \qquad C_2 = ? \qquad T = 373 \text{ K}$$
$$\frac{dL}{dT} = -0{\cdot}64 \text{ cal/K}$$
$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$
$$C_2 = C_1 + \frac{dL}{dT} - \frac{L}{T}$$
$$= 1{\cdot}01 + (-0{\cdot}64) - \frac{540}{373}$$
$$= \mathbf{-1{\cdot}077 \text{ cal/g}}$$

It shows that the specific heat of saturated steam is negative.

Example 6·45. *Calculate the specific heat of saturated steam at 100°*C *from the following data :*

*L at 90°*C = *545·25* cal

*L at 100°*C = *539·30* cal

*L at 110°*C = *533·17* cal

Specific heat of water at 100°C = 1·013 cal/g

[*Delhi 1975*]

Here
$$\frac{dL}{dT} = \frac{533{\cdot}17 - 545{\cdot}25}{20}$$
$$= \frac{-12{\cdot}08}{20} = -0{\cdot}604 \text{ cal/K}$$
$$L = 539{\cdot}3 \text{ cal}$$
$$T = 373 \text{ K}$$

$$C_1 = 1{\cdot}013$$

$$C_2 = ?$$

$$C_2 - C_1 = \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = C_1 + \frac{dL}{dT} - \frac{L}{T}$$

$$C_2 = 1{\cdot}013 - 0{\cdot}604 - \frac{539\ 3}{373}$$

$$C_2 = -\mathbf{1{\cdot}036\ cal/g}$$

Example 6·46. *Using Maxwell's thermodynamical relations, prove that for any substance, the ratio of the adiabatic and isothermal elasticities is equal to the ratio of the two specific heats.*

From definition,

Isothermal elasticity $E_T = -V\left(\frac{\partial P}{\partial V}\right)_T$

Adiabatic elasticity $E_S = -V\left(\frac{\partial P}{\partial V}\right)_S$

$$\therefore \qquad \frac{E_S}{E_T} = \frac{-V\left(\frac{\partial P}{\partial V}\right)_S}{-V\left(\frac{\partial P}{\partial V}\right)_T}$$

$$= \frac{\left(\frac{\partial P}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial V}\right)_T}$$

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_S \left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial V}\right)_T}$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_S}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial S}{\partial V}\right)_T} \qquad \ldots(i)$$

But from the first four Maxwell's equations

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

∴ Substituting these values in equation (i)

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial S}\right)_V}{\left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial S}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial H}{\partial T}\right)_P}{\left(\frac{\partial H}{\partial T}\right)_V}$$

But $\left(\frac{\partial H}{\partial T}\right)_P = C_P$

and $\left(\frac{\partial H}{\partial T}\right)_V = C_V$

$$\therefore \quad \frac{E_S}{E_T} = \frac{C_P}{C_V} = \gamma \qquad \text{...(iii)}$$

Example 5.47 *Using Maxwell's thermodynamical relations, prove that the ratio of the adiabatic to the isobaric coefficient of expansion is*

$$\frac{1}{(1-\gamma)}$$

Adiabatic volume coefficient of expansion,

$$\alpha_S = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S \qquad \text{...(i)}$$

Isobaric volume coefficient of expansion,

$$\alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{...(ii)}$$

$$\therefore \quad \frac{\alpha_S}{\alpha_P} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_S}{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P} \qquad \text{...(iii)}$$

$$= \frac{\left(\frac{\partial V}{\partial T}\right)_S}{\left(\frac{\partial V}{\partial T}\right)_P} = \frac{1}{\left(\frac{\partial T}{\partial V}\right)_S \left(\frac{\partial V}{\partial T}\right)_P}$$

But
$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$\therefore$
$$\frac{\alpha_S}{\alpha_P} = -\frac{1}{\left(\frac{\partial P}{\partial S}\right)_V\left(\frac{\partial V}{\partial T}\right)_P}$$

$$= \frac{1}{-\left[\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial S}\right)_V\left(\frac{\partial V}{\partial T}\right)_P\right]}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_V}{-\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P}$$

$$= \frac{T\left(\frac{\partial S}{\partial T}\right)_V}{-T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P}$$

But
$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

and
$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$\therefore$
$$\frac{\alpha_S}{\alpha_P} = \frac{C_V}{-(C_P - C_V)}$$

or
$$\frac{\alpha_S}{\alpha_P} = \frac{1}{1-\left(\frac{C_P}{C_V}\right)}$$

or
$$\frac{\alpha_S}{\alpha_P} = \frac{1}{1-\gamma} \qquad \text{..(iv)}$$

Example 6·48. *Using Maxwell's thermodynamical relations, prove that the ratio of the adiabatic to the isochoric pressure coefficient of expansion is equal to*

$$\frac{\gamma}{(\gamma-1)}$$

Adiabatic pressure coefficient of expansion,

$$\beta_S = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S \qquad \text{...(i)}$$

Isochoric pressure coefficient of expansion.

$$\beta_V = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \qquad \text{...(ii)}$$

$\therefore$
$$\frac{\beta_S}{\beta_V} = \frac{\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_S}{\frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V} \qquad \text{...(iii)}$$

$$= \frac{\left(\frac{\partial P}{\partial T}\right)_S}{\left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{1}{\left(\frac{\partial T}{\partial P}\right)_S \left(\frac{\partial P}{\partial T}\right)_V}$$

But $$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_I \qquad \ldots(iv)$$

$$\frac{\beta_S}{\beta_V} = \frac{1}{\left(\frac{\partial V}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V} \qquad \ldots(v)$$

$$= \frac{1}{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{\left(\frac{\partial S}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{T\left(\frac{\partial S}{\partial T}\right)_P}{T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

$$= \frac{C_P}{C_P - C_V}$$

or $$\frac{\beta_S}{\beta_V} = \frac{\left(\frac{C_P}{C_V}\right)}{\left(\frac{C_P}{C_V} - 1\right)} = \frac{\gamma}{\gamma - 1} \qquad \ldots(vi)$$

Example 6·49. *Using Maxwell's thermodynamical relations, show that*

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial V . \partial T}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

From Maxwell's relations,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(i)$$

Differentiating equation (*i*) with respect to temperature,

$$\left(\frac{\partial^2 S}{\partial T . \partial V}\right) = \left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad \ldots(ii)$$

But $$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \qquad \ldots(iii)$$

Differentiating equation (*iii*) with respect to volume,

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial V}\right) \qquad ...(iv)$$

From equations (*ii*) and (*iv*)

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 S}{\partial T.\partial V}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad ...(v)$$

Example 6·50. *Using Maxwell's thermodynamical relations, show that*

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial P \partial T}\right) = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

From Maxwell's relations,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad ...(i)$$

Differentiating equation (*i*) with respect to temperature

$$\left(\frac{\partial^2 S}{\partial T \partial P}\right) = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad ...(ii)$$

But $\qquad C_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad ...(iii)$

Differentiating equation (*iii*) with respect to pressure,

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T \partial P}\right) \qquad ...(iv)$$

From equations (*ii*) and (*iv*)

$$\left(\frac{\partial C_P}{\partial P}\right) = T\left(\frac{\partial^2 S}{\partial T \partial P}\right) = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \qquad ...(v)$$

Example 6·51 *Show that for a perfect gas*

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From the Maxwell's first equation,

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{1}{T}\left(\frac{\delta H}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

or $$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

But $\qquad \delta H = dU + PdV$

$$\therefore \left(\frac{dU + PdV}{dV}\right) = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{dU}{dV} + P = T\left(\frac{\partial P}{\partial T}\right)_V$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

But from perfect gas equation,

$$PV = RT$$

$$\therefore \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

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

or $$\left(\frac{\partial U}{\partial V}\right)_T = P - P = 0$$

$$\therefore \quad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Exercises VI

1. Deduce the adiabatic equation for an ideal gas and give Clement and Desormes' method for determining γ.
(Agra 1960 ; Delhi 1972, 73)

2. State the Second Law of thermodynamics. Describe Carnot's cycle and deduce the efficiency of an ideal heat engine.
(Agra 1960, 61, 62)

3. Explain what you understand by thermodynamic scale of temperature. Show that it agrees with an ideal gas scale. What is zero on this scale ? *(Agra 1962)*

4 Derive Clapeyron's latent heat equation.

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$ *(Delhi 1974; Agra 1972)*

5. State and prove Carnot's theorem. *(Agra 1963)*

6. Define Entropy. What is its physical significance ? Show that the entropy of a perfect gas remains constant in a reversible process but increases in an irreversible process.
(Agra 1963 ; Delhi 1971, 73)

7. Prove that

$$\frac{dL}{dT} - \frac{L}{T} = C_2 - C_1$$

What is the physical significance of negative specific heat ?
(Agra 1963)

8. Prove that PV^γ = constant in an adiabatic transformation.
(Madras 1974 ; Agra 1972 ; Delhi 1976)

9. What do you understand by the absolute scale of temperature ? Show that the zero and the size of the degree on this scale and the gas scale are coincident. Is a negative temperature possible on this scale ?

10. Prove the thermodynamic relation

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$$

Hence show that the increase of pressure heats a body that expands with rise of temperature and cools the one that contracts on heating. (*Agra 1964*)

11. Describe with diagrams the working of an Otto engine and deduce an expression for its efficiency.

12. Prove the thermodynamical relation

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

and hence show that

$$L = T(V_2-V_1)\left(\frac{dP}{dT}\right) \qquad \text{(Agra 1965)}$$

13. State the two laws of thermodynamics and explain their significance. Derive an expression for the efficiency of a Carnot's engine. (*Delhi 1976, Agra 1966*)

14. Define Kelvin's absolute or thermodynamic scale of temperature. Show how this scale agrees with that of a perfect gas scale. Is a negative temperature possible on this scale ? (*Agra 1966*)

15. Derive the relation between volume and pressure of a gas undergoing adiabatic changes. (*Rajasthan 1960*)

16. Derive an expression for the efficiency of an ideal heat engine, working between the temperatures T_1 and T_2K. Prove that the efficiency of a reversible engine is maximum for the given source and sink. (*Rajasthan 1961 ; Delhi 1972*)

17. Discuss the Second Law of Thermodynamics and the principle of increase of entropy. (*Rajasthan 1964*)

18. Explain fully what you understand by entropy. Show that the change in entropy of a substance in a cyclic process is zero (*Panjab 1964*)

19. Deduce Clapeyron's equation. How does it explain the effect of pressure on (*i*) the melting point of solids and (*ii*) the boiling point of liquids.
(*Berhampur 1972 ; Panjab 1963 ; Delhi [Hons.] 1971*)

20. What is a reversible thermodynamic process ? Describe a reversible heat engine and find an expression for its efficiency. (*Lucknow 1963*)

21. State Carnot's theorem. Show how Kelvin used this theorem to define a new scale of temperature which is independent of the nature of the working substance. Compare this temperature scale with the perfect gas scale. (*Berhampur 1972 ; Lucknow 1962, 64*)

22. Describe the absolute scale of temperature. Why is it adopted as the standard scale ? What is the meaning of absolute zero on the scale ? *(Delhi 1961 [Sub] 1966)*

23. Explain the concept of entropy. Deduce the expression for the entropy of a monoatomic gas. *(Delhi 1966)*

24. Derive an expression for the efficiency of a Carnot's engine in terms of the temperatures of the source and the sink. Show how an absolute scale of temperature can be defined with the help of the ideal Carnot's engine *(Punjab 1966)*

25. Deduce Clausius Clapeyron's equation *(Delhi 1967)*

26 Deduce the Clapeyron's latent heat equation from Maxwell's thermodynamical relations

27. Deduce Maxwell's thermodynamical relations. *(Delhi [Hons.] 1971)*

28. Show that *(Delhi [Hons.] 1976)*

(*i*) $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(*ii*) $\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$

(*iii*) $\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P$

(*iv*) $\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial S}\right)_V$

(*v*) $\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial H}\right)_P$

(*vi*) $\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P\left(\frac{\partial S}{\partial P}\right)_V = 1$

and (*vii*) $\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial V}{\partial T}\right)_S = 1$

29 Show that for a homogeneous fluid

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$$

30. Show from the consideration of Maxwell's thermodynamical relations that

(*i*) for a perfect gas

$$C_P - C_V = R$$

and (*ii*) for a gas obeying Van der Waals equation

$$C_P - C_V = R\left(1 + \frac{2a}{RTV}\right)$$

31 Derive the specific heat relation

$$C_P - C_V = -TE\alpha^2 V$$ [*Delhi (Hons) 1971*]

32. What do you understand by the internal energy of a system? State the first law of thermodynamics and use it to derive a relation between the volume and temperature of a perfect gas undergoing an adiabatic change of state (*Delhi 1969*)

33 Deduce Clausius-Clapeyron's equation and discuss the effect of change of pressure on the melting and boiling points of a substance (*Delhi 1968, 71, 76*)

34 Deduce the Clausius Clapeyron's equation for the change of equilibrium pressure of two phases with temperature (*Delhi 1969, 1972*)

35. Describe Partington's method for the determination of the ratio of the two specific heats of a gas (*Delhi 19[illegible]*)

36 What are isothermal and adiabatic changes? Derive the equation PV^{γ} = constant for an ideal gas (*Delhi 1971*)

37. What is meant by a reversible process? Describe the Carnot cycle and show that all reversible engines working between the same two temperatures have the same efficiency [*Madras 19[illegible]1, Delhi 19[illegible]*]

38 Calculate the work done in a Carnot's cycle of operation. Deduce the efficiency of a Carnot's engine in terms of the temperatures between which it works (*Delhi 1973*)

39 Define entropy. State and prove the principle of increase of entropy

40. Define work scale of temperature. Show that the ideal gas scale and the work scale are identical [*Delhi 1971*]

41 Show that

$$\int_A^B \frac{\delta Q}{T}$$ is independent of the path for a reversible change [*Delhi (Hons) 1977*]

42 Calculate the change in entropy when m grams of a liquid of specific heat S is heated from T_1 K to T_2 K and then converted into vapour without raising its temperature. Latent heat of vaporisation at T_2 is L [*Delhi (Hons) 1961*]

43 Show that

$$\frac{\left[\frac{\partial P}{\partial T}\right]_S}{\left[\frac{\partial P}{\partial T}\right]_V} = \frac{\gamma}{\gamma - 1}$$

[*Delhi (Hons) 1971, 1976*]

44. What is meant by thermodynamical equilibrium? Discuss the equilibrium between a liquid and its vapour and hence deduce Clausius-Clapeyron's equation. [*Delhi (Hons) 1972*]

45 Explain the concepts of reversible and irreversible processes. Obtain an expression for the efficiency of a reversible Carnot engine with a perfect gas as the working substance. Show that for the same pair of working temperatures the efficiency of all reversible engines is the same and is the maximum value attainable.

[*Delhi 197[illegible], Delhi (Hons) 1973*]

46 Show how the second law of thermodynamics enables us to define a scale of temperature independent of the properties of any working substance. How is the scale realised in practice?

[*Delhi (Hons), 197[illegible]*]

47 Derive Maxwell's thermodynamical equations and show that

$$C_P - C_V = -T\left[\frac{\partial V}{\partial T}\right]_P^2\left[\frac{\partial P}{\partial V}\right]_T$$

[*Delhi (Hons) 1972*]

48 Describe in detail Clement and Desorme's method of finding the ratio of the two specific heats of a gas giving the simple theory of the method. What are the objections to the method and what modifications and improvements have been proposed?

[*Delhi 1975, 76, 77*]

49 Establish the relation connecting the temperature and the volume of a gas undergoing adiabatic compression. [*Delhi 1975*]

50 Establish the latent heat equation

$$\frac{dL}{dT} - \frac{L}{T} = C_2 - C_1$$

where C_1 and C_2 are the specific heat of the liquid and its saturated vapour respectively. [*Delhi 197[illegible], 197[illegible]*]

51 Explain the term entropy and discuss its properties. Show that the entropy of a system tends to a maximum. Represent the Carnot cycle on a temperature-entropy diagram and prove that its area represents available energy. Establish directly from the above considerations that the efficiency of the engine is

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

[*Delhi 1975*]

52 Define entropy. What is its physical significance? Show that the entropy remains constant in a reversible process. What happens in case the process is an irreversible one?

[*Delhi 197[illegible]*]

53 Enunciate the second law of thermodynamics. Define a temperature scale without making use of the peculiarities of any selected thermometric substance. Show that Kelvin's work scale is such a scale and that the ratio of the two temperatures as measured on the Kelvin scale is identical with the ratio of the same two temperatures on a perfect gas scale. [*Delhi 1975*]

54 State the first law of thermodynamics and use it to derive a relation between pressure and temperature of a perfect gas undergoing an adiabatic change [*Delhi, 1974*]

55 Under suitable conditions the Joule-Thomson effect results in cooling and so does an adiabatic expansion of a gas

Distinguish between these two types of cooling
[*Delhi 1974, Rajasthan 197[illegible]*]

56 Deduce the following Maxwell's relations

(i) $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

(ii) $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

[*Delhi (Hons.) 1974*]

57 With the help of appropriate Maxwell's relations show that for a substance

$$C_P - C_V = TVE\alpha^2$$

[*Rajasthan, 1975, Delhi (Hons.) 1974*]

58 State Carnot's theorem and deduce it from the second law of thermodynamics [*Kanpur, 1975, Delhi (Hons.) 1974*]

59 Derive the Clausius Clapeyron's latent heat equation for first order phase changes

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

[*Agra 1975, Delhi (Hons.) 1974, Delhi 1976*]

60 Distinguish between isothermal and adiabatic changes. Show that for an adiabatic change in a perfect gas

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

[*Delhi (Hons.) [illegible]*]

61 What do you understand by the Kelvin's thermodynamic scale of temperature ? Prove that the ratio of two temperatures on the thermodynamic scale is identical with the ratio of the same two temperatures measured on the perfect gas scale
[*Delhi, 19[illegible], Delhi (Hons.) 197[illegible], 197[illegible]*]

62 Explain what you mean by entropy of a substance. Show that the entropy remains constant in a reversible process but increases in an irreversible process
[*Kanpur, 1975 Delhi (Hons.) 1975*]

63 Prove that

$$\frac{E_S}{E_T} = \gamma$$

[*Delhi (Hons.) 1975*]

64 State the first law of thermodynamics. Express it mathematically and explain its physical significance
[*Delhi (Additional Physics), 1975*]

65. Deduce the first latent heat equation. Discuss how the boiling point of a liquid and the melting point of a solid are affected by change of pressure. [*Bombay, 1974*]

66. Describe Carnot's cycle and obtain an expression for the efficiency of an ideal heat engine in terms of temperatures. [*Bombay, 1974*]

67. Derive the relation between the volume and temperature of a perfect gas undergoing adiabatic compression. [*Delhi, 1976*]

68. Explain what you mean by entropy of a substance. Show that for any reversible cyclic change of a system, the total change of entropy is zero. Show that this statement is not true for an irreversible change. [*Delhi, 1977*]

69. Discuss the equilibrium between a liquid and its vapour and hence deduce Clausius Clapeyron's equation. Explain, how the boiling point of a liquid and the melting point of a solid are affected by change of pressure. [*Delhi (Hons.) 1977*]

70. Derive Maxwell's first and second thermodynamical relations and deduce the Clausius Clapeyron's latent heat equation from Maxwell's second relation. [*Kanpur 1975*]

71. Define Carnot's cycle. Explain the working of a Carnot's heat engine. Calculate its efficiency when a perfect gas is the working substance. [*Rajasthan, 1975*)

72 What is meant by the order of a phase change ? Discuss it giving examples. [*Delhi (Hons), 1977*]

State and discuss Zeroth law of thermodynamics. [*Delhi, 1978*]

73 Define isothermal and adiabatic transformations. Give examples.

Obtain equation of state for an ideal gas undergoing (*i*) an isothermal transformation and (*ii*) an adiabatic transformation. [*Delhi, 1978*]

74. Dry air at N. T. P. (normal temperature and pressure) is compressed adiabatically to one-third of its original volume. Calculate the resulting pressure. Given that the ratio C_p/C_v of air is 1·40 [*Delhi, 1978*]

75. What is the importance of Clausius-Clapeyron latent heat equation ? Derive this equation and outline its applications. [*Delhi, 1978*]

76. For a quasi-static adiabatic process of an ideal gas, prove

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

[*Delhi (Hons.), 1978*]

77. State Carnot's Theorem and show that it is a necessary consequence of Second Law of Thermodynamics. Prove that the efficiency of a Carnot engine using an ideal gas as a working substance is $\eta = \frac{T_1-T_2}{T_1}$. [*Delhi (Hons), 1978*]

78 Derive the following relations :

(a) $C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T$

(b) $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

(c) $\frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{\gamma}{\gamma-1}$ [*Delhi (Hons.), 1978*]

79 Write short notes on

(i) Isothermal Process
(ii) Adiabatic Process
(iii) Isochoric Process
(iv) Carnot's engine
(v) Carnot's theorem [*Delhi, 1975*]
(vi) Second Law of thermodynamics
(vii) Clement and Desormes' method
(viii) Ruchhardt's experiment for γ
(ix) Absolute gas scale
(x) Rankine cycle
(xi) Diesel engine
(xii) Steam engine
(xiii) Otto cycle
(xiv) Entropy is a measure of disorder
(xv) Entropy tends to a maximum
(xvi) Third Law of thermodynamics
(xvii) Absolute zero temperature
(xviii) Entropy of a perfect gas [*Delhi (Hons.) 1977*]
(xix) Temperature-Entropy diagram
(xx) Thermodynamic system
(xxi) Thermal Equilibrium
(xxii) Concept of Temperature
(xxiii) Concept of Heat
(xxiv) Zeroth Law in Thermodynamics
(xxv) Phase changes of the second order [*Delhi (Hons.), 1975*]

80 A motor car tyre has a pressure of 3 atmospheres at the room temperature of 27°C. If the tyre suddenly bursts what is the resulting temperature ? [**Ans** 218.6 K = −54.4°C]

81 A quantity of air ($\gamma = 1.4$) at 27°C is compressed suddenly to ¼ of its original volume. Find the final temperature.
[**Ans** 522.3 K = 249.3°C]

82 A quantity of air at 27°C and atmospheric pressure is suddenly compressed to ⅕ of its original volume. Find (i) the final pressure and (ii) the final temperature.
[**Ans** (i) 8.29 atmospheres (ii) 571.1 K = 298.1°C]

83 Find the efficiency of the Carnot's engine working between 150°C and 50°C. [**Ans.** 23·64%]

84. Find the efficiency of a Carnot's engine working between 227°C and 27°C. [**Ans.** 40%]

85. A Carnot's engine whose temperature of the source is 400 K takes 500 calories of heat at this temperature and rejects 400 calories of heat to the sink. What is the temperature of the sink? Calculate the efficiency of the engine.

[**Ans.** (*i*) 320 K, (*ii*) 20%]

86. A Carnot's engine is operated between two reservoirs at temperatures of 500 K and 400 K. If the engine receives 2000 calories of heat from the source in each cycle, calculate (*a*) the amount of heat rejected to the sink in each cycle, (*b*) the efficiency of the engine and (*c*) the work done by the engine in each cycle in (*i*) joules (*ii*) kilo-Watt hours

[**Ans** (*a*) 1600 calories, (*b*) 20%, (*c*) (*i*) 1780 joules, (*ii*) $4·941 \times 10^{-4}$ kWh]

87. A Carnot's engine working as a refrigerator between 250 K and 300 K receives 1000 calories of heat from the reservoir at the lower temperature (*i*) Calculate the amount of heat rejected to the reservoir at the higher temperature. (*ii*) Calculate also the amount of work done in each cycle to operate the refrigerator.

[**Ans.** (*i*) 1200 cal, (*ii*) 840 joules]

88. Calculate the depression in the melting point of ice produced by 2 atmospheres increase of pressure. Given latent heat of ice = 80 cal/g and the specific volumes of 1 gram of ice and water at 0°C are 1·091 cm³ and 1·000 cm³ respectively.

[**Ans.** 0·0148 K or 0·0148°C]

89. Find the increase in the boiling point of water at 100°C when the pressure is increased by 2 atmospheres. Latent heat of vaporisation of steam is 540 cal/g and 1 g of steam occupies 1677 cm³ volume. [**Ans.** 55·84 K or 55·84°C]

90. Calculate the change in the melting point of naphthalene for 2 atmospheres rise in pressure, given that its melting point is 80°C. Latent heat of fusion is 4563 cal/mol and increase in volume on fusion is 18 [illegible] cm³/mol. 1 cal = 4·2 × 10^7 ergs.

[**Ans.** −0·06976 K or −0·06976°C]

91. Calculate the temperature at which ice will freeze if the pressure is increased by 135·2 atmospheres. The change in specific volume when 1 gram of water freezes into ice is 0·091 cm³. One atmospheric pressure = 10^6 dynes/cm². Latent heat of fusion of ice = 80 cal/g. and $J = 4·2 \times 10^7$ ergs/cal [**Ans.** −1·0°C]

92. Calculate the temperature at which water will boil if the pressure is increased by 1·814 atmospheres. Given that the change in specific volume when one gram of water is converted into steam is 1676 cm³. Latent heat of vaporization of steam = 540 cal/g. $J = 4·2 \times 10^7$ ergs/cal and one atmosphere pressure = 10^6 dynes/cm².

[**Ans.** 150°C]

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.

$$\left[\textbf{Ans.}\ \ 2{\cdot}774\ \frac{R}{J}\ \text{cal/K}\right]$$

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 cm³. $J = 4{\cdot}2\times10^7$ ergs/cal. One atmosphere = 10^6 dynes/cm². 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*) $8{\cdot}75\times10^{24}$ 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	-116°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.

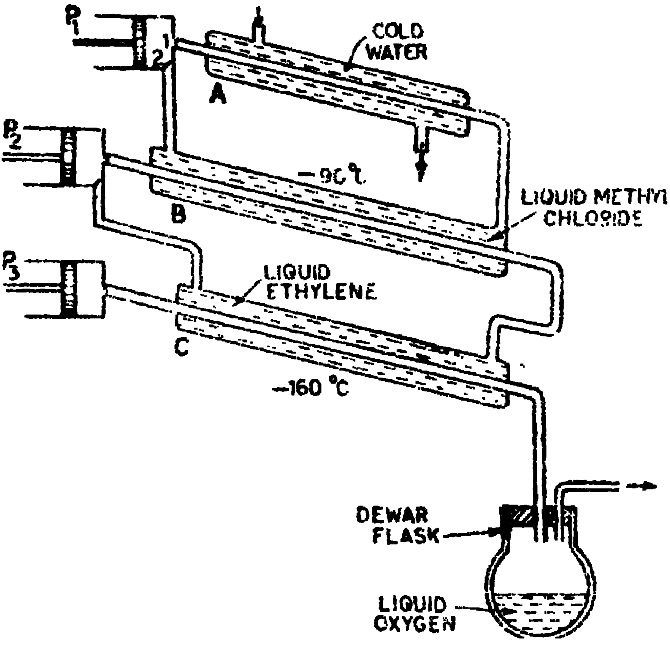


Fig. 7·1

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_2 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.

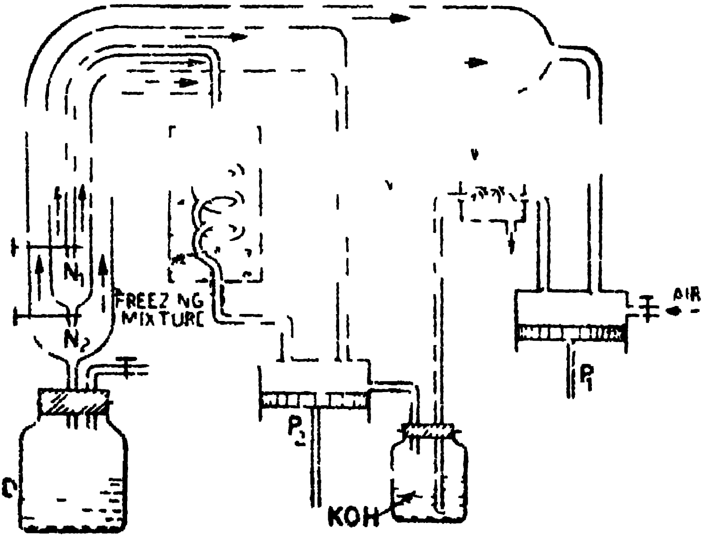


Fig. 7.2

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. The 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. The air passes through a spiral tube surrounded by a jacket containing freezing mixture. The 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. The 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 is 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 recirculated 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 as designed by Dewar (1898) was improved 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*

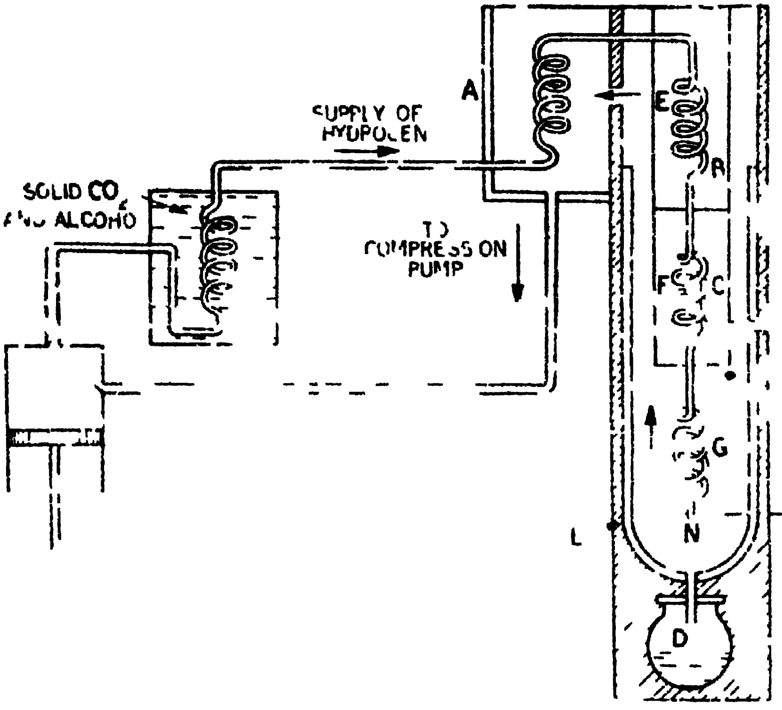


Fig 7 3

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 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.

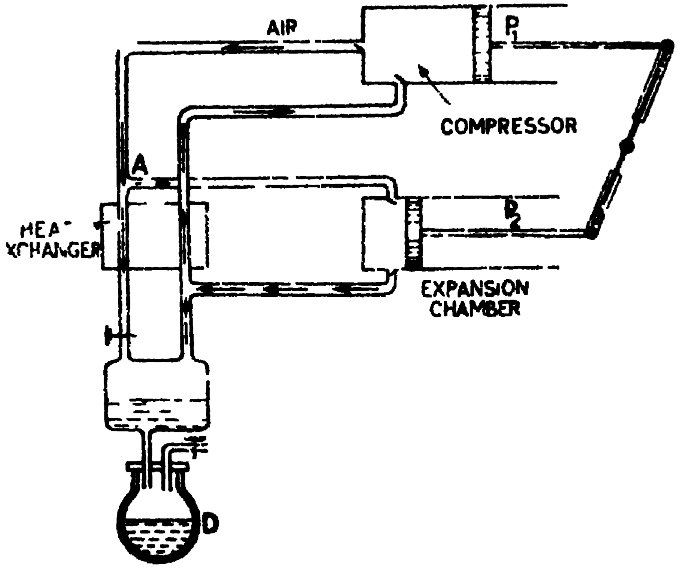


Fig. 7·4

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 tube at A. It is divided in 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_1 and S_2 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

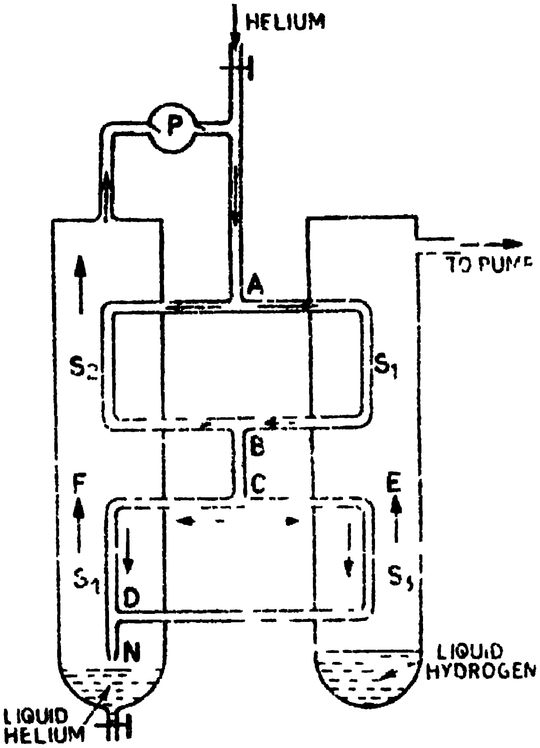


Fig. 7·5

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

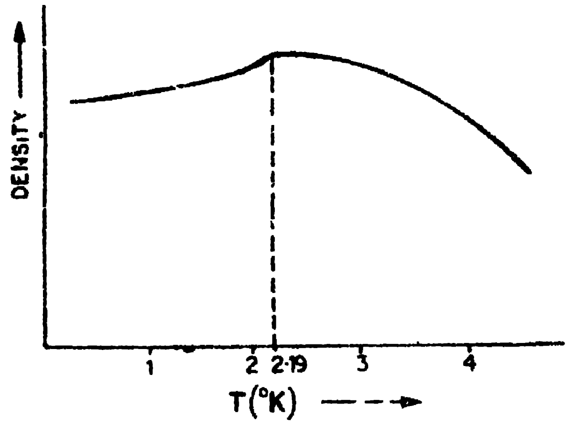


Fig 7·6

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

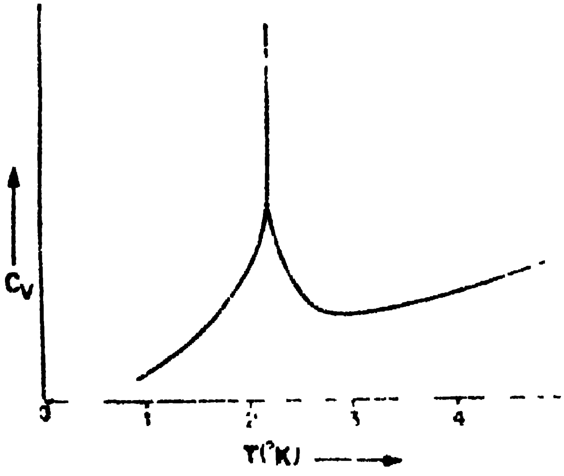
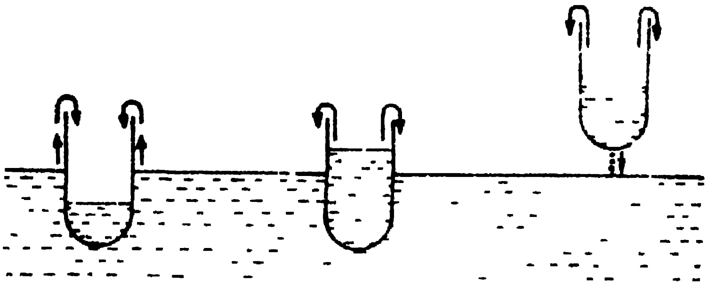


Fig. 7·7

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



(i) (ii) (iii)

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 [illegible] 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.

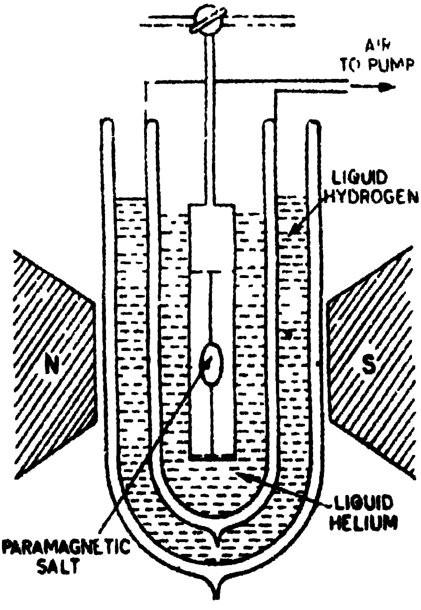


Fig. 7·9

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

$$\chi T \text{ is constant}$$

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

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.

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

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.

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

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.

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

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)

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

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

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

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

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

When the magnetic field is switched off,

$$B_f = 0$$

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

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

$$\Delta T = \frac{CV B_i^2}{2\,C_B T_i} \qquad \ldots(xii)$$

7.11 Conversion of Magnetic Temperature to Kelvin Temperature

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

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

As the change in volume is negligible,

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

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

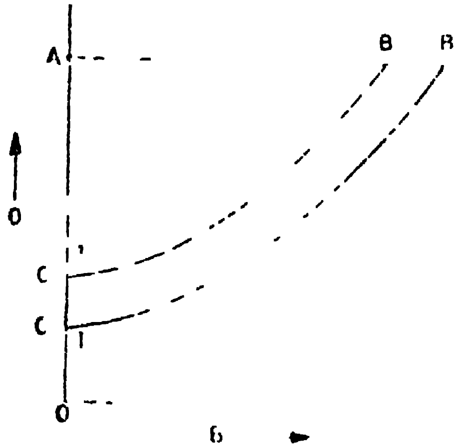


Fig. 7·10

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 [illegible] 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).

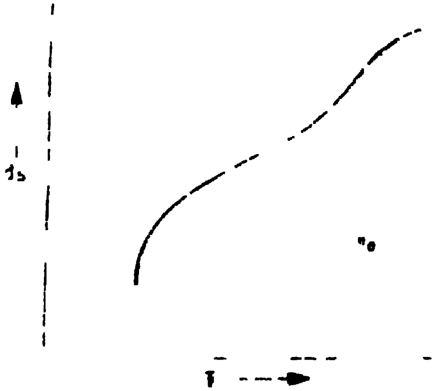


Fig. 7·11.

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

To determine the value of $\left(\dfrac{\partial U}{\partial T}\right)_{B\to 0}$, 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)

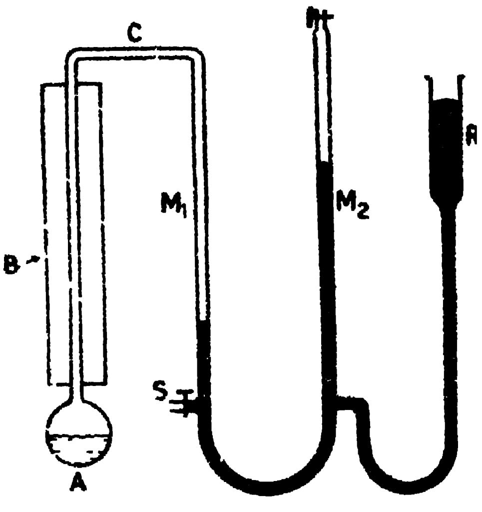


Fig. 7·12

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 pressure 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	23·1
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.

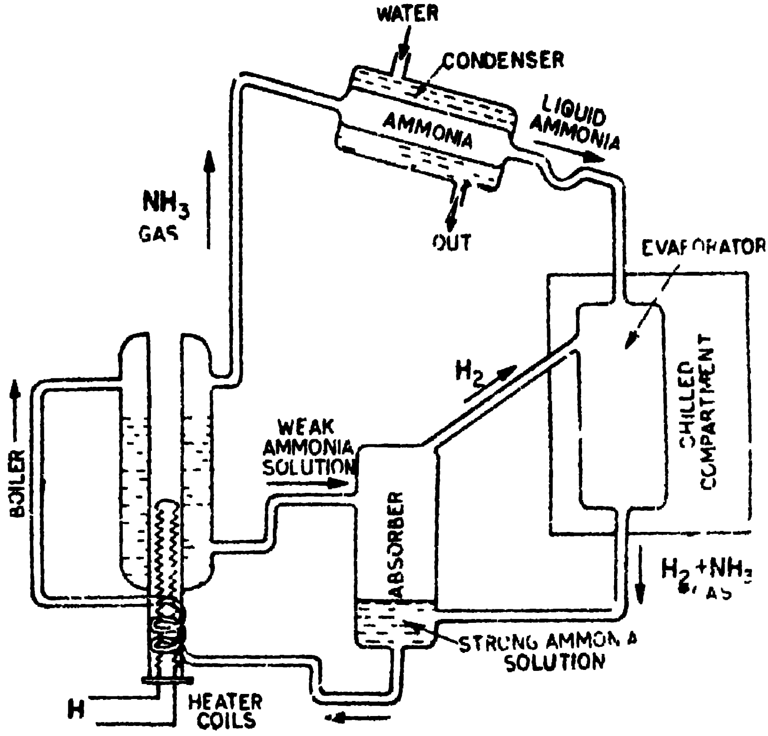


Fig 7·13

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 1973*)

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 1976*]

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

$$Q \propto A$$

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

$$Q \propto t$$

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

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

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

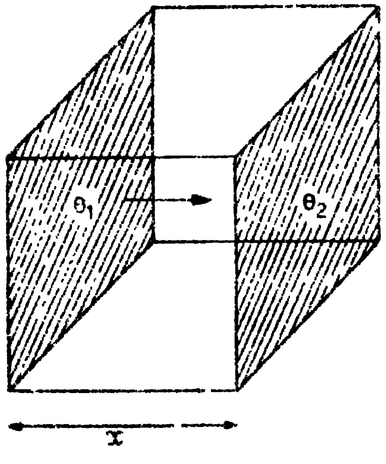


Fig. 8·1

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.

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

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 a which is heated at one end. Heat is flowing along the length of the bar. Consider two

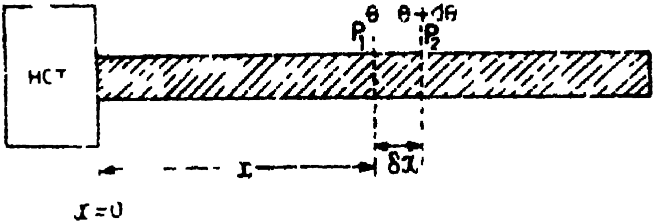


Fig. 9.2

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

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

Heat flowing through P_2 in one second

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

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

$$Q = Q_1 - Q_2$$

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

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

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

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

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

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

$$= Ep\,\delta x\,\theta \qquad \text{...(v)}$$

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

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

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

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

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

Special Cases

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

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

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

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

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

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

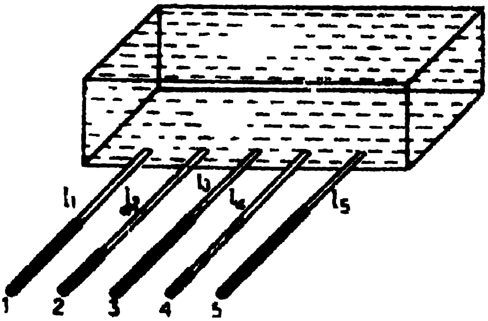


Fig 8 3

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 of 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,

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

$$\ldots\ldots\ldots\ldots\ldots\ldots$$

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

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

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

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

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,

$$l_1 = 10 \text{ cm}$$

$$l_2 = 4 \text{ cm}$$

$$K_1 = 0.90$$

$$K_2 = ?$$

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

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

$$= \frac{16}{100} \times 0.90$$

$$K_2 = 0.144$$

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).

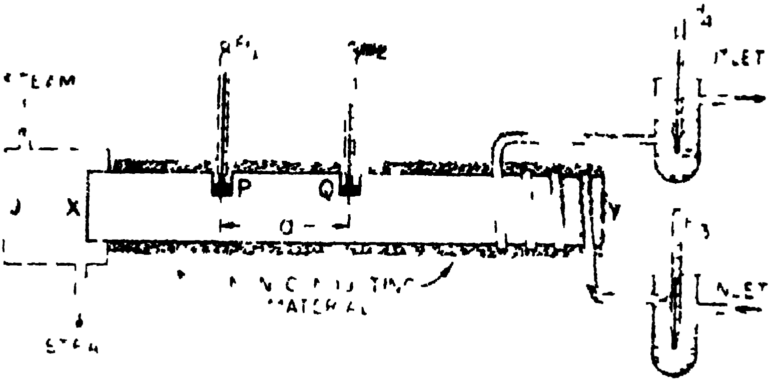


Fig. 8.4

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,

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

Amount of heat gained by water in one second

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

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

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

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

Knowing all the quantities, K can be calculated.

Example 8·2. *The opposite faces of a metal plate of 0·2 cm thickness 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
$$K = 0{\cdot}2$$
$$A = 200 \text{ sq cm}$$
$$d = 0{\cdot}2 \text{ cm}$$
$$(\theta_1-\theta_2) = 100°\text{C}$$
$$t = 60 \text{ s}$$
$$Q = \frac{KA(\theta_1-\theta_2)t}{d}$$
$$= \frac{0{\cdot}2\times200\times100\times60}{0{\cdot}2}$$
$$= \mathbf{12\times10^5 \text{ cal}}$$

Example 8·3. *A bar of length 20 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*)

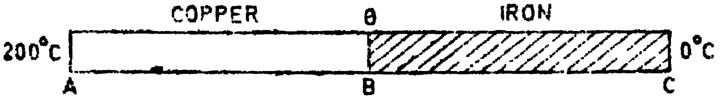


Fig. 8·5.

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

$$\therefore \qquad \frac{K_1 A\,(200-\theta)}{d} = \frac{K_2 A\,(\theta-0)}{d}$$

$$0{\cdot}9\,(200-\theta) = 0{\cdot}12\,\theta$$

$$\theta = 176{\cdot}5°\text{C}$$

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

$$\therefore \qquad Q = \frac{K_1 A\,(\theta_1-\theta)}{d}$$

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

or

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

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

$$\therefore \qquad \frac{K_1 A\,(12-\theta)}{d_1} = \frac{K_2 A\,(\theta-0)}{d_2}$$

Here

$$K_1 = 0{\cdot}0006,\ K_2 = 0{\cdot}00012$$

$$d_1 = 1{\cdot}75 \text{ cm},\ d_2 = 3 \text{ cm}$$

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

$$\theta = 10{\cdot}74°\text{C}$$

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

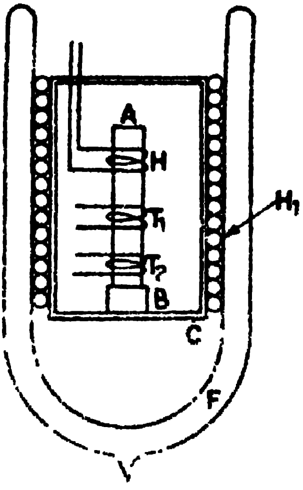


Fig. 8·6

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 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

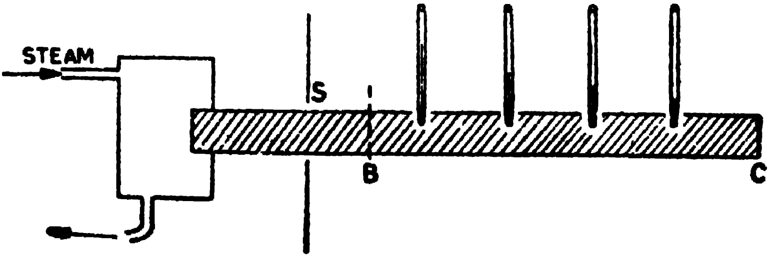


Fig. 8·7.

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

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

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

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

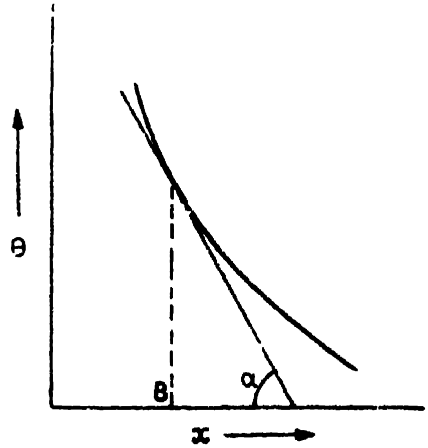


Fig. 8·8

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

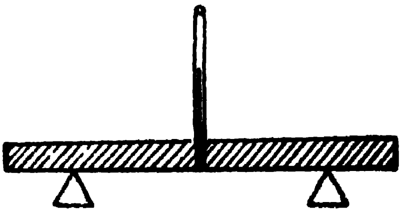


Fig. 8·9

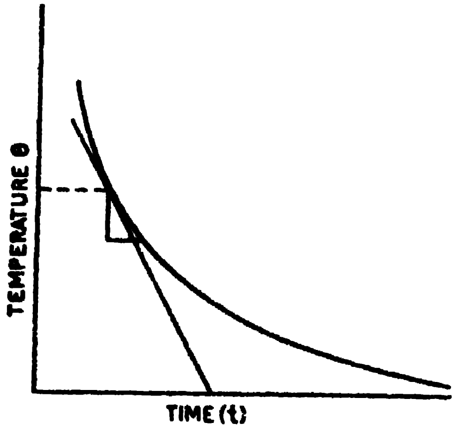


Fig. 8·10

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.

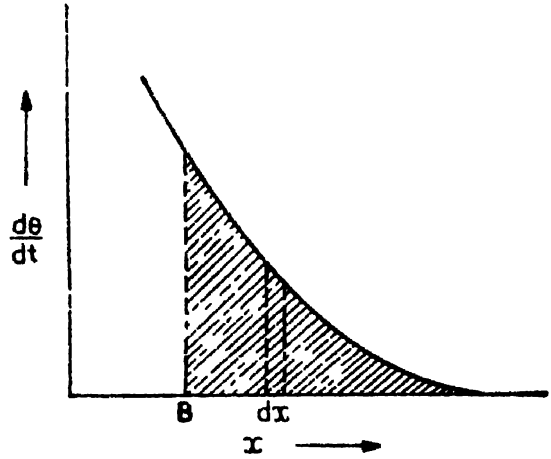


Fig. 8 11

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

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

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 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.

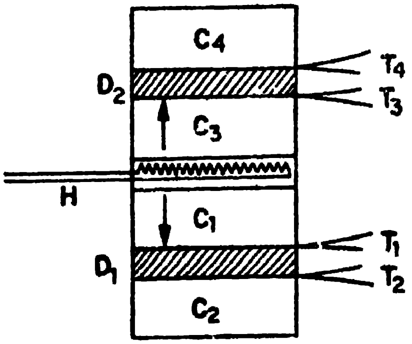


Fig. 8·12

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_2 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 $\left[\dfrac{A+S}{2A+S}\right]$ 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, $\dfrac{d\theta}{dt}$ is the rate of cooling at temperature θ_2, m is the mass and s is the specific heat of C.

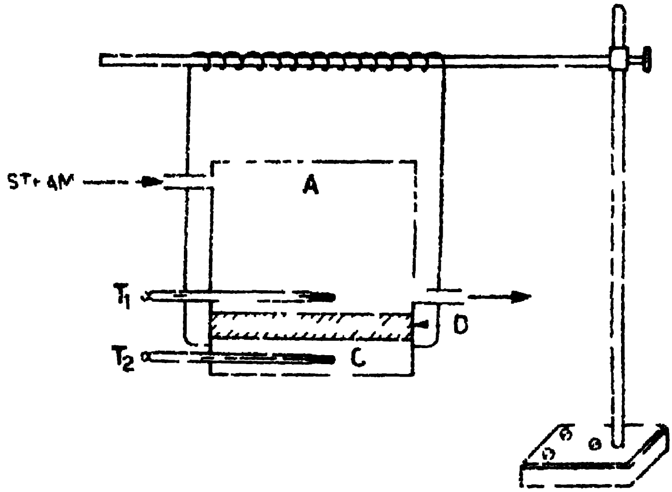


Fig. 8.15

To find $\dfrac{d\theta}{dt}$, 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 at equal intervals of time (say one minute). A graph is drawn between temperature and time. From the graph, the value of $\dfrac{d\theta}{dt}$ 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.

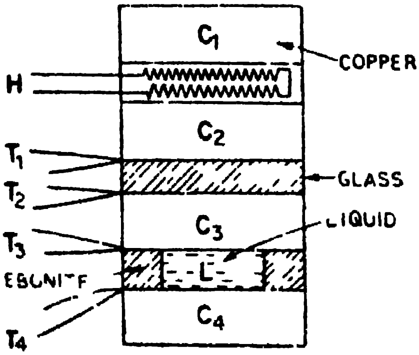


Fig 8·14

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

$$= \frac{K_1 A_1(\theta_3-\theta_4)}{d_1} + \frac{K_2 A_2(\theta_3-\theta_4)}{d_1} \qquad \ldots(ii)$$

Equations (i) and (ii)

$$\therefore \quad \frac{KA(\theta_1-\theta_2)}{d} = \frac{K_1 A(\theta_3-\theta_4)}{d_1} + \frac{K_2 A_2(\theta_3-\theta_4)}{d_1} \qquad \ldots(iii)$$

The value of K_1 for the liquid can be calculated from equation (iii). However, there is a small error due to the heat lost by the sides of 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. 8.17). 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.

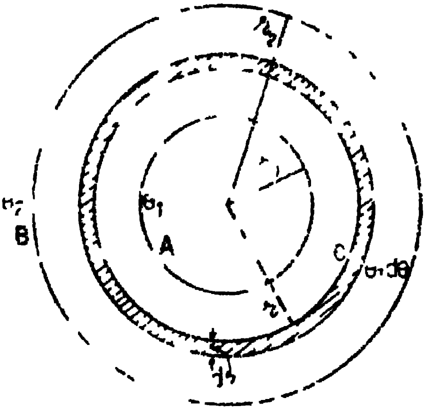


Fig. 8.17

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

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

Here $A = 4\pi r^2$

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

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

Integrating,

$$\int_{r_1}^{r_2}\frac{dr}{r^2} = -\frac{4\pi K}{Q}\int_{\theta_1}^{\theta_2} d\theta$$

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

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

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)

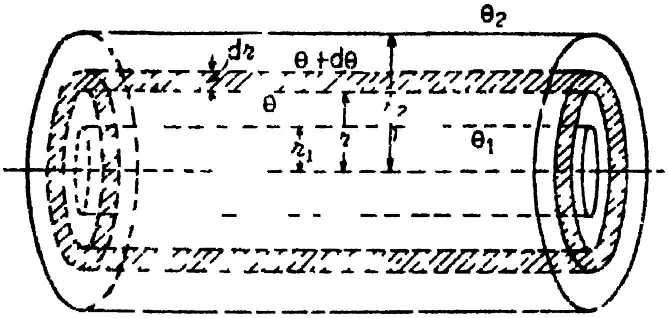


Fig. 8.16

The quantity of heat flowing per second across the element

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

But $$A = 2\pi rl$$

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

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

Q is constant after the steady state is reached

Integrating equation (i)

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

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

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

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

or $$K = \frac{Q\times 2.3026\times\log_{10}\frac{r_2}{r_1}}{2\pi l(\theta_1 - \theta_2)} \qquad \text{(iii)}$$

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

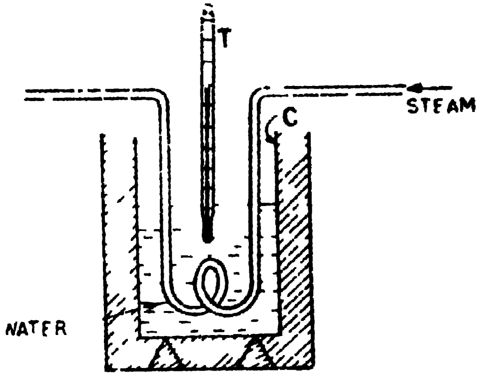


Fig. 8 17

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.

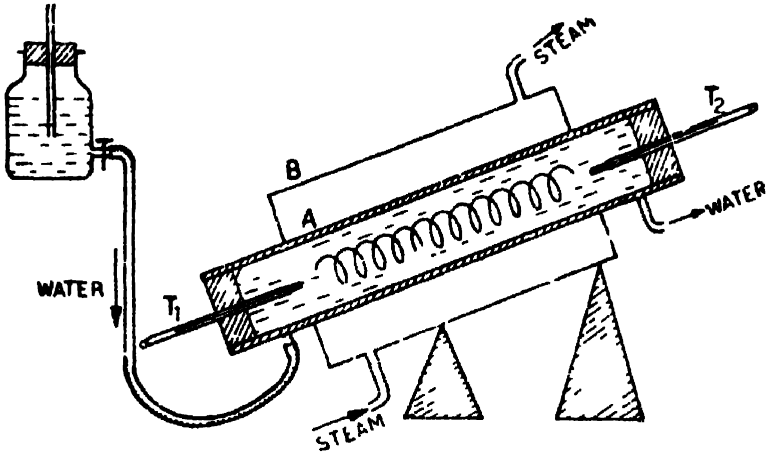


Fig 8·18

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 = θ_1

Temperature of incoming water = θ_3

Temperature of outgoing water = θ_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
$$K = \frac{Q\times 2\cdot3026\times\log_{10}\left(\frac{r_2}{r_1}\right)}{2\pi l\left(\theta_1-\frac{\theta_3+\theta_4}{2}\right)}\,t \qquad \ldots(i)$$

Substituting the values of Q in equation (i)

$$\therefore\quad K = \frac{m(\theta_4-\theta_3)\times 2\cdot3026\log_{10}\left(\frac{r_2}{r_1}\right)}{2\pi l\left(\theta_1-\frac{\theta_3+\theta_4}{2}\right)t} \qquad \ldots(ii)$$

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 co-efficients 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.

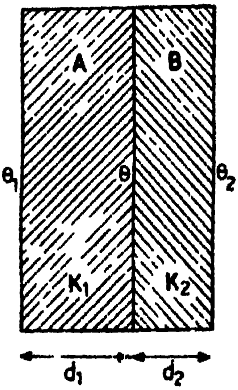


Fig. 8 19

For the material A,

$$Q = \frac{K_1A(\theta_1-\theta)}{d_1} \qquad \ldots(i)$$

For the meterial B,

$$Q = \frac{K_2A\,(\theta-\theta_2)}{d_2} \qquad \ldots(ii)$$

From equations (i) and (ii),

$$\frac{K_1A\,(\theta_1-\theta)}{d_1} = \frac{K_2A\,(\theta-\theta_2)}{d_2}$$

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

Substituting the value of θ in equation (i),

$$Q = \frac{A(\theta_1 - \theta_2)}{\frac{d_1}{K_1} + \frac{d_2}{K_2}} \qquad \text{.. (iii)}$$

In general, for any number of walls or slabs,

$$Q = \frac{A(\theta_1 - \theta_2)}{\sum\left(\frac{d}{K}\right)} \qquad \text{..(iv)}$$

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 in contact with the surface of ice be $-\theta$ °C and that

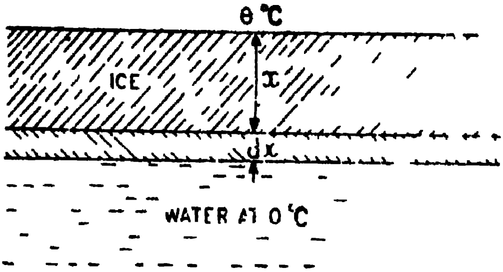


Fig 8 20

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

$$= A\,dx\,\rho\,L \text{ calories} \qquad \text{...(i)}$$

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

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

Equating (i) and (ii)

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

$$\frac{dx}{dt} = \frac{K\theta}{\rho L x} \qquad \text{...(iii)}$$

$\frac{dx}{dt}$ 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

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

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

When $t = 0,\ x = 0$

Hence the constant is zero.

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

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)*

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

$$t = \frac{\rho L}{2K\theta}\left[r_2^2 - r_1^2\right]$$

Here

$\rho = 0{\cdot}91$ g/cm³

$L = 80$ cal/g

$K = 0{\cdot}005$

$\theta = 20°$C

$r_1 = 3$ cm

$r_2 = 3{\cdot}1$ cm

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

$$= 222{\cdot}01 \text{ s}$$

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

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

$$= 9\times 10^4 \text{ s} = \mathbf{25\ hours}$$

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 the 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 $\frac{K}{\sigma T} \times 10^8$

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	2·48

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 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.

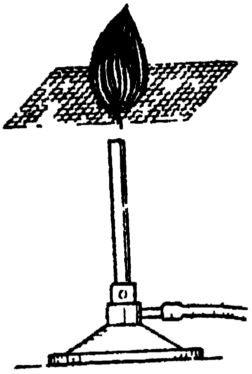


Fig. 8·21

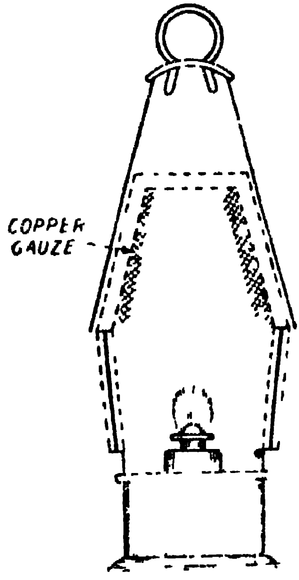


Fig. 8·22

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

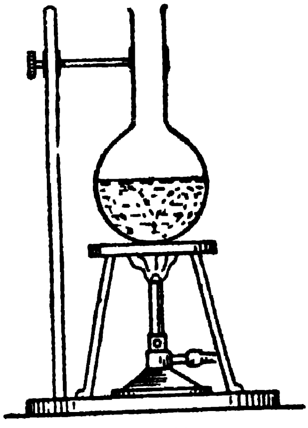


Fig. 8·23

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.

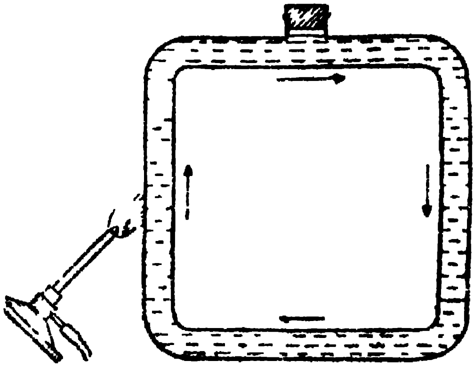


Fig. 8·24

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

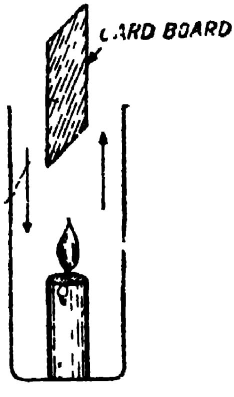


Fig. 8·25

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 based on the principle of convection.

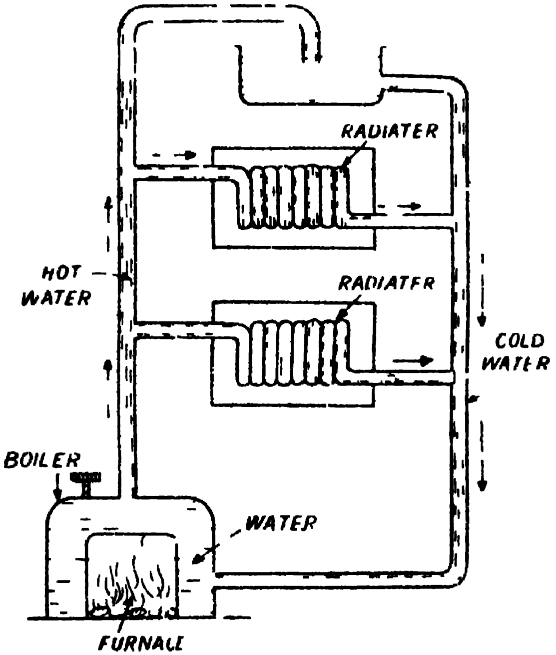


Fig. 8·26

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).

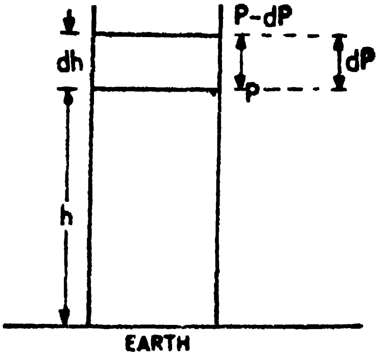


Fig. 8·27

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

[$-ve$ 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 $$V = \frac{RT}{P}$$

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

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

Integrating

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

When $$h = 0,$$

$$P = P_0$$

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

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*)

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

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

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 [illegible] 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 $P^{\gamma-1}T^{-\gamma}$

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

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

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

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

But $$PV=RT$$

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

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

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

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

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

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

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

Substituting the values,

$$M = 29 \text{ g}$$
$$g = 981 \text{ cm/s}^2$$
$$R = 8{\cdot}31 \times 10^7 \text{ ergs per gram mol per K,}$$

and

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

$$\frac{dT}{dh} = -\frac{29 \times 981}{8{\cdot}31 \times 10^7}\left(\frac{1{\cdot}40-1}{1{\cdot}40}\right)$$
$$= 10^{-4} \text{ K per cm}$$
$$= 10^{-4} \,^\circ\text{C per cm}$$

Thus the lapse rate for a height of 1 km $= 10^{-4} \times 10^5 = 10$°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 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).

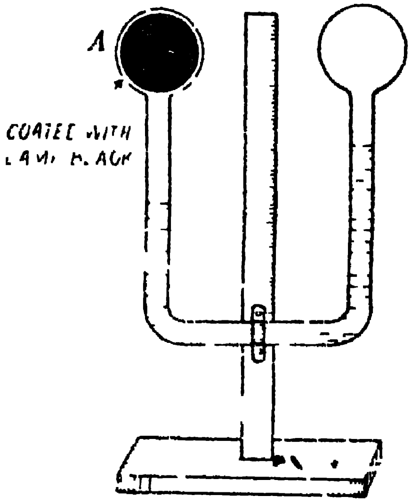


Fig. 8·28

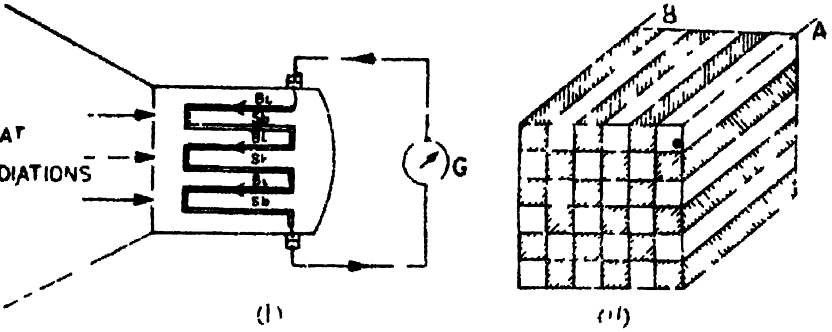
When *A* is exposed to heat radiations, it absorbs heat energy. Air inside the bulb *A* expands and there is difference in level of the liquid in the two limbs. This thermoscope is very sensitive and can detect heat radiations of even feeble intensity (*i.e.*, from a candle at a large distance).

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 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



(i) (ii)

Fig 8 [illegible]

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

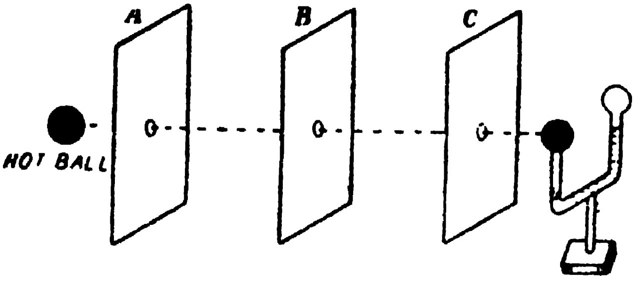


Fig. 8·30

(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 he 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.

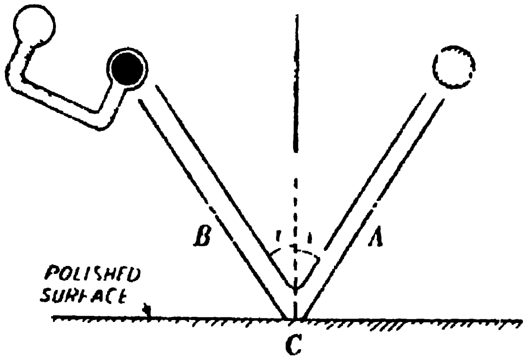


Fig 8·31

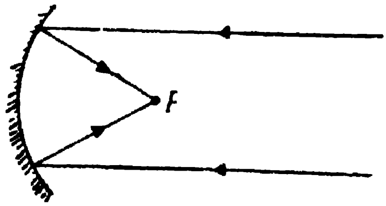


Fig. 8·32

(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 sealed. The inner surface of *B* and the outer surface of *A* are highly polished (*i.e.* silvered) (Fig. 8·33).

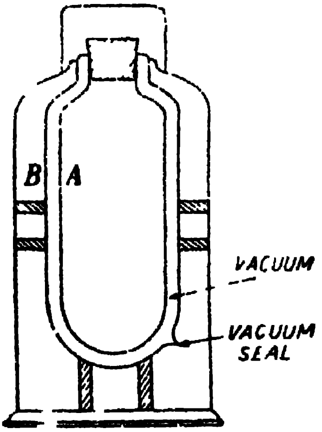


Fig. 8·33

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.

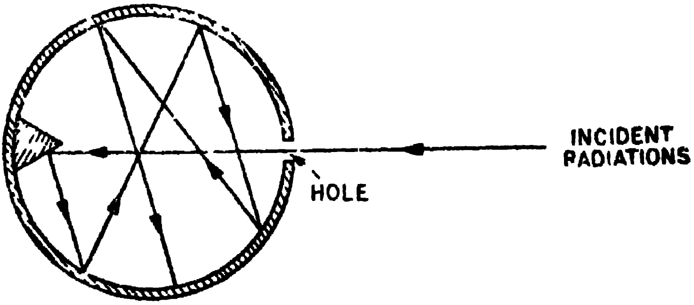
Similarly ice kept inside the flask will not melt for a long time because heat radiations from outside cannot enter the inside of the bottle.

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.

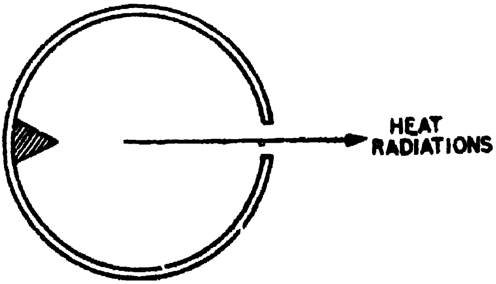
In practice, a perfectly black body is not available. A body showing close approximation to a perfectly black body can be constructed.

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 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 absorber

Fig 8 34



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.

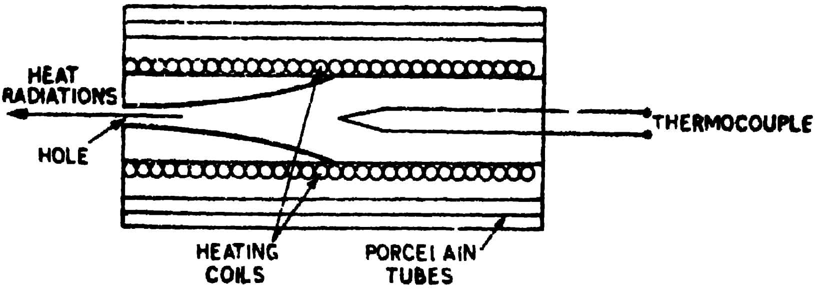


Fig 8·36

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

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

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

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

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

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

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

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.

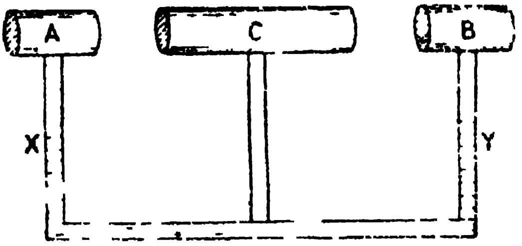


Fig. 8·37

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.

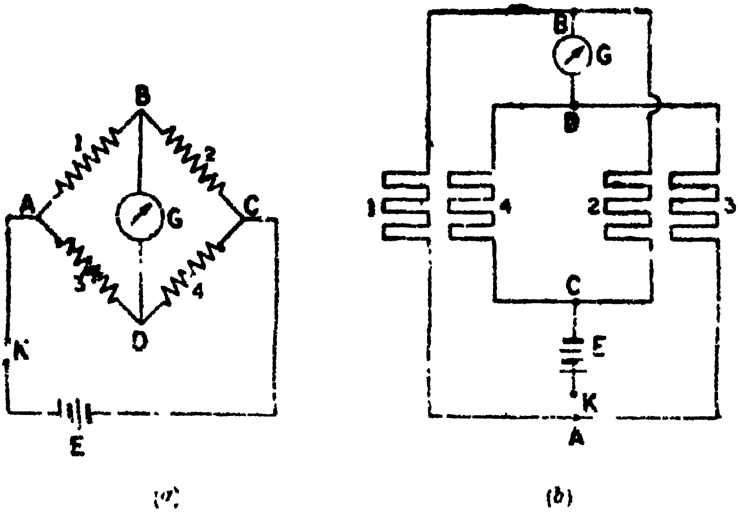
8·32 Prevost Theory of Heat Exchange

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



(a) (b)

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 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.

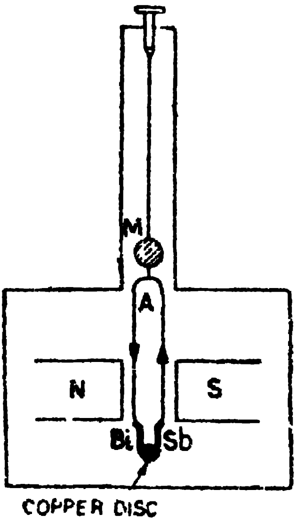


Fig. 8·39

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

Here $T_1 = 300$ K

$T_2 = 200$ K

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

$R = \sigma[T_1^4 - T_2^4]$

$= 5\,672 \times 10^{-8}[(300)^4 - (200)^4]$

$R =$ **368·68 watts/m²**

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) $R = 5\,672 \times 10^{-8}\,[400]^4$

$=$ **1452 watts/m²**

(ii) $R = 5\,672 \times 10^{-8}\,[4000]^4 = 1452 \times 10^4$ watts/m²

$=$ **14520 kilo watts/m²**

Example 8.9. *The relative emittance of tungsten is approximately 0.35. A tungsten sphere of surface area 10^{-2}* 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 2000* K? *The conduction of heat along the supports can be neglected.* [$\sigma = 5.672 \times 10^{-8}$ M.K.S. units]

$R = $ [illegible] $[T^4 - T_0^4]$

Here $A = 10^{-2}$ sq metres

$e = 0.35$

$\sigma = $ [illegible] M.K.S. units

$R = 5.672 \times 10^{-8} \times 10^{-2}$

$\times 0.35 \times [(2000)^4 - (300)^4]$

1609 watts

The power input = **1609 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.* [$\sigma = 5.672 \times 10^{-8}$ M.K.S. units]

Here $T_1 = 300$ K

$T_2 = 200$ K

$e = 0.1$

$\sigma = 5.672 \times 10^{-8}$ 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 $$[(300)^4 - x^4] = [x^4 - (200)^4]$$

$$x^4 = 48.5 \times 10^8$$

$$\mathbf{x = 263.8\ K}$$

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

$$R = 0.1 \times 5.672 \times 10^{-8}[(300)^4 - (263.8)^4]$$

$$R = \mathbf{18.5\ watts/m^2}$$

Example 8.11. *Calculate the energy radiated per minute from the filament of an incandescent lamp at 2000* K, *if the surface area is 5.0×10^{-5}* sq metres *and its relative emittance is 0.85.*

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

$A = 5 \times 10^{-5}$ m²

$e = 0.85$

$\sigma = 5.672 \times 10^{-8}$ M.K.S. units

$$t = 60\ \text{s}$$

$$T = 2000\ \text{K}$$

$$E = 5 \times 10^{-5} \times 0.85 \times 5.672 \times 10^{-8} \times 60 \times (2000)^4$$

$$E = \textbf{2315 joules}$$

Example 8.12 *An open furnace radiates 1.53 × 10⁶ 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* $\sigma = 1.36 \times 10^{-8}$ cal/m² s K⁴

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

$$E = 1.53 \times 10^6\ \text{calories}$$

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

$$e = 0.80$$

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

$$T = ?$$

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

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

$$= \left[\frac{1.53 \times 10^6}{10^{-4} \times 0.80 \times 1.36 \times 10^{-8} \times 3600}\right]^{\frac{1}{4}}$$

$$T = \textbf{2500 K}$$

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

$$\delta H = dU + P.dV \qquad \text{...(i)}$$

Applying thermodynamical relation

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \text{...(ii)}$$

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{...(iii)}$$

Now $\quad U = V\psi$

and $\quad P = \dfrac{\psi}{3}$

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, $\log\psi = 4\log T + \text{constant}$

or $$\psi = KT^4 \qquad \ldots(iv)$$

Here K is a constant

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

$$\therefore \qquad R \propto \psi \propto T^4$$

$$\therefore \qquad R = \sigma T^4 \qquad \ldots(v)$$

where σ is Stefan's constant.

The value of Stefan's constant in C.G.S. system is 5.672×10^{-5} C.G.S. units and in M.K.S. system it is 5.672×10^{-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 $4e\sigma T_2^3 = k$

$$R = k(T_1 - T_2)$$

or $$R \propto (T_1 - T_2) \qquad \ldots(ii)$$

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 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).

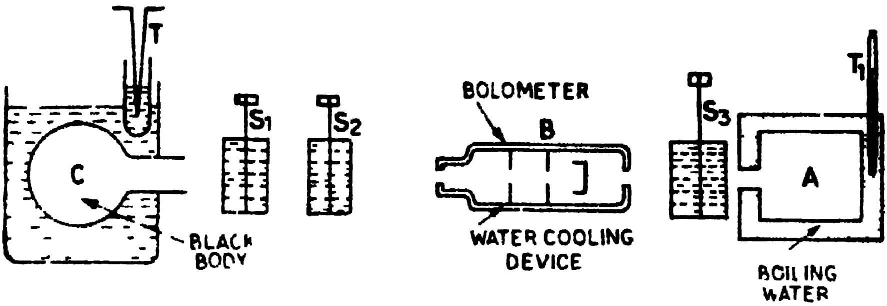


Fig. 8·40

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 $\quad \theta \propto R$

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

This verifies Stefan's law.

Recently Coblentz has verified Stefan's law more accurately. He took an electrically heated black body whose temperature was measured by an accurate thermocouple. An absolute bolometer was used to measure the amount of heat radiations emitted by the black body. He was able to show the correctness of Stefan's law experimentally up to 1600°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

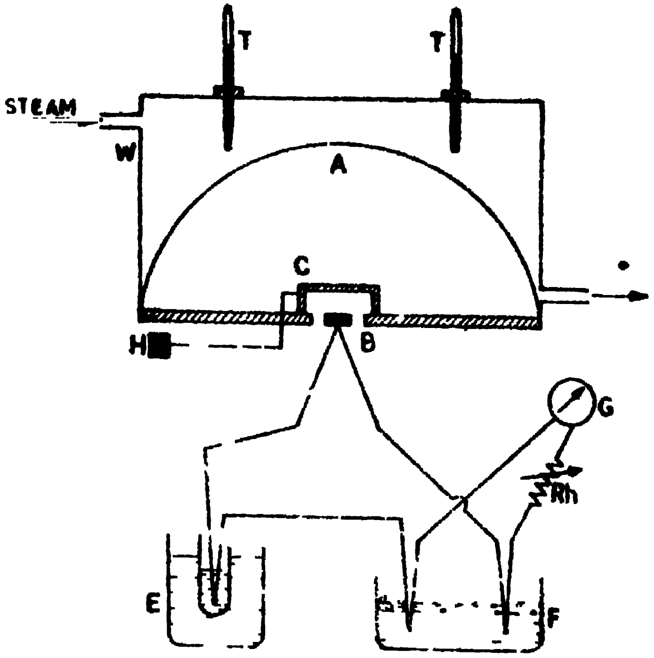


Fig. 8.41

A is enclosed in a wooden box *W*. The inner surface of *A* is coated with lamp black and the wooden box 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. 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 placing it into the chamber [illegible] The

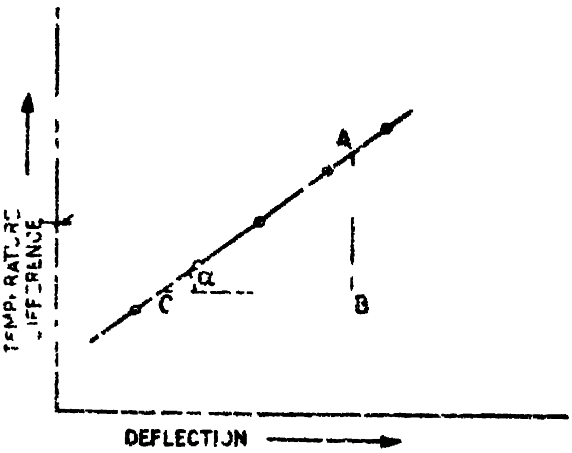


Fig. 8.42

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 [illegible] axis and [illegible] deflection [illegible] Y axis is plotted (Fig. 8.42). From the graph,

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

2. The disc is completely covered with a lid. 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 [illegible] is lifted 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 to the curve at a point P.

$$\frac{d\theta}{dt} = \tan\beta = \frac{PF}{GF} \qquad \text{...(ii)}$$

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,

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

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

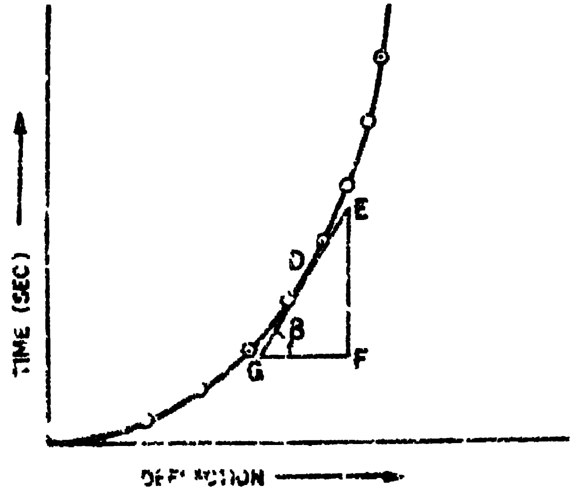


Fig. 8·43

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.

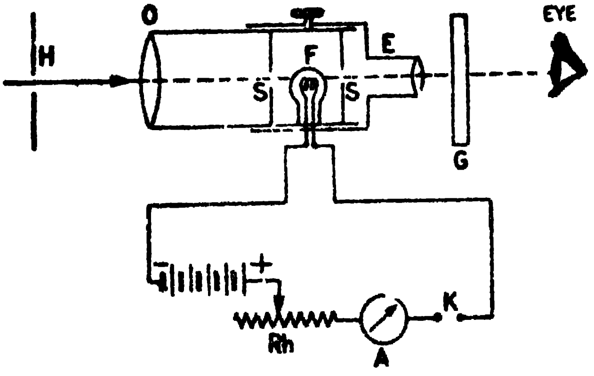


Fig 8·44

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).

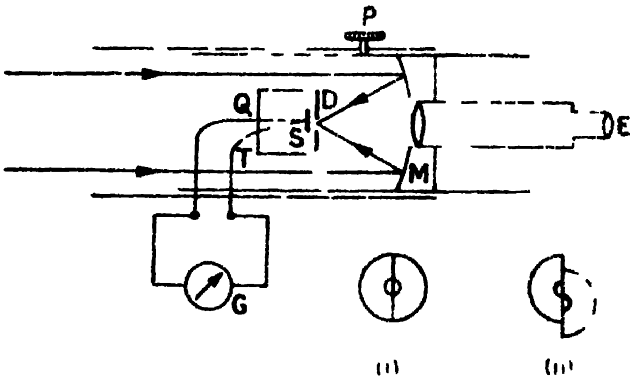


Fig. 8.45

When the radiation is incident on the mirror, the focussed image falls on the opening of D. Due to the incident radiation 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 8.45 (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 galvanometer 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.

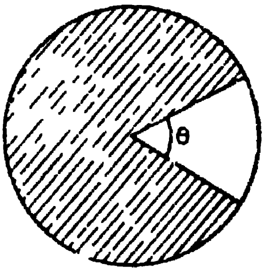


Fig. 8.46

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 the 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

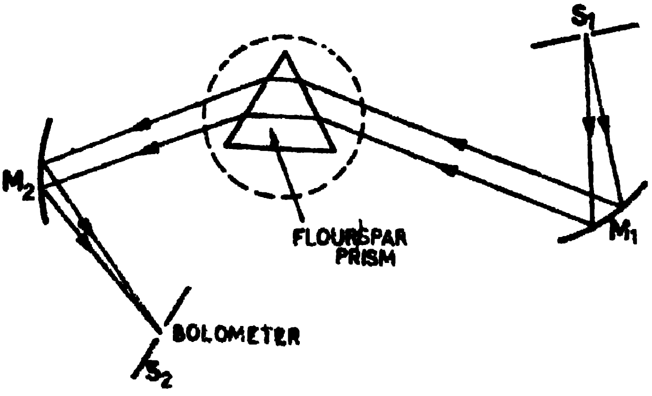


Fig. 8 47

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

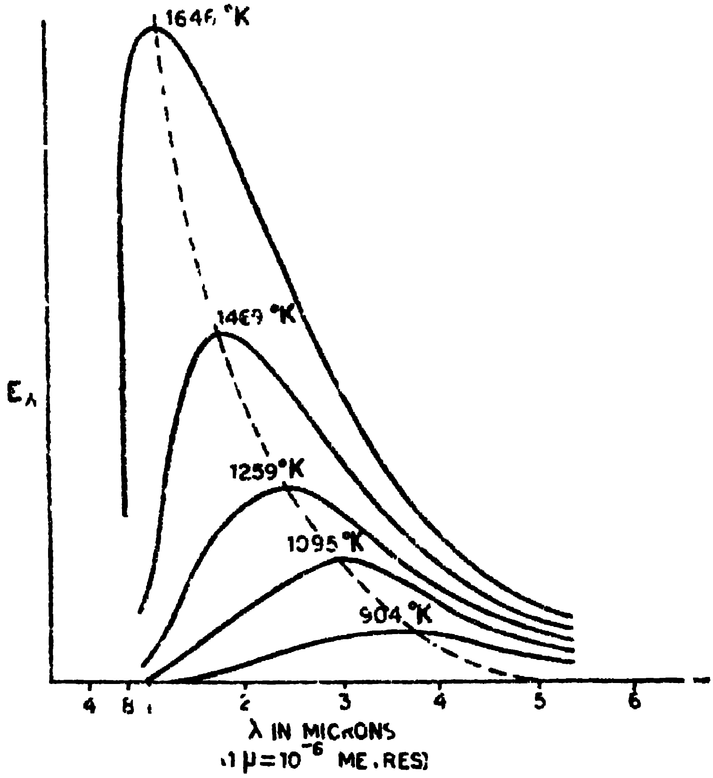


Fig. 8·48

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. 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 expresses 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

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

Here k is the Boltzmann's constant

The experimental results of Lummer and Pringsheim in the infrared 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,

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

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

Equation (vi) agrees with the experimental results

(i) For shorter wavelengths

$$\frac{h\nu}{kT} \gg 1$$

From equation (vi),

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

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

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

Equation (vii) represents Wien's radiation law

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

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

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

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

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

Equation (viii) represents Rayleigh Jeans's law.

Thus Planck's formula for the energy distribution in the 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 pyrheliometer. 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

$$S = S_0 a^{\sec Z} \qquad \text{...(i)}$$

or

$$\log S = \log S_0 + \sec Z \log a \qquad \text{...(ii)}$$

Here a is a constant.

A graph is plotted between $\log S$ along the y-axis and $\sec Z$ along the x-axis. The graph is a straight line. Produce the graph to meet the y axis. The intercept on the y-axis gives $\log S_0$. From the value of $\log S_0$, the value of S_0, the solar constant can be calculated. The value obtained varies between 1.90 and [illegible] 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 cm² 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 $R = 148.48 \times 10^7$ km

$r = 6.928 \times 10^5$ km

The mean value of

$S = 1.94$ cals per cm² per minute

$$E = \left(\frac{148.48 \times 10^7}{6.928 \times 10^5}\right)^2 \times \frac{1.94}{60} \text{ cal per second} \quad \ldots(i)$$

Also $E = \sigma T^4$

But $\sigma = 5.75 \times 10^{-5}$ ergs per cm² per second

$$= \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} \text{ cal per cm}^2 \text{ per second}$$

$$E = \frac{5.75 \times 10^{-5}}{4.2 \times 10^7} \cdot T^4 \quad \ldots(ii)$$

Equating (i) and (ii)

$$\left(\frac{5.75 \times 10^{-5}}{4.2 \times 10^7}\right) T^4 = \left(\frac{148.48 \times 10^7}{6.928 \times 10^5}\right)^2 \times \frac{1.94}{60}$$

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

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,

$$\lambda_{max} T = 0.2892$$

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 $= 1.37 \times 10^{-12}$ 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

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

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

$$S = 2{\cdot}3 \text{ cal/cm}^2\text{/minute}$$

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

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

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. ...(*i*)

Heat produced in one minute in the strip *B*

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

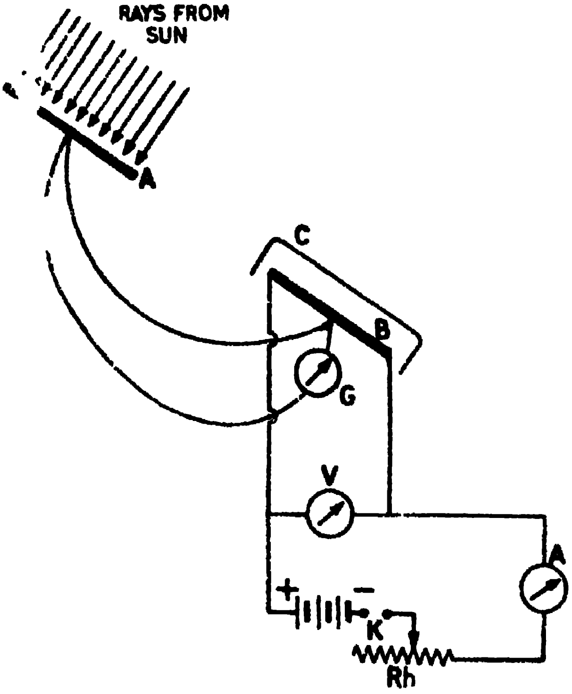


Fig. 8·49

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 . 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 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 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.

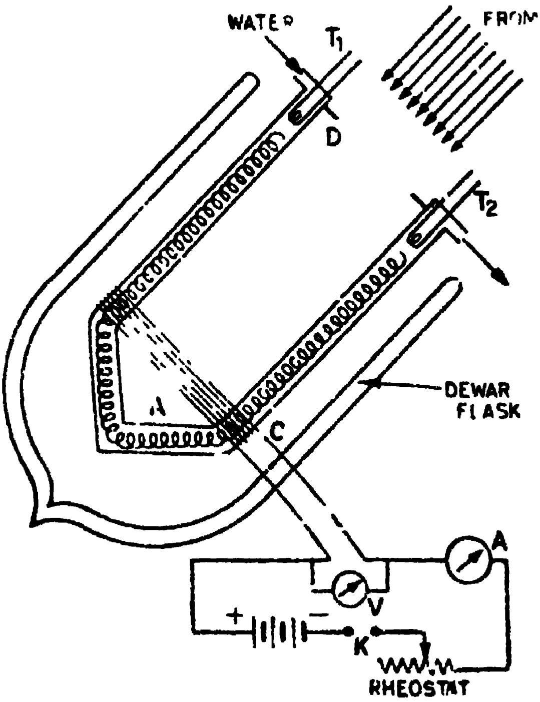


Fig. 8·50

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.

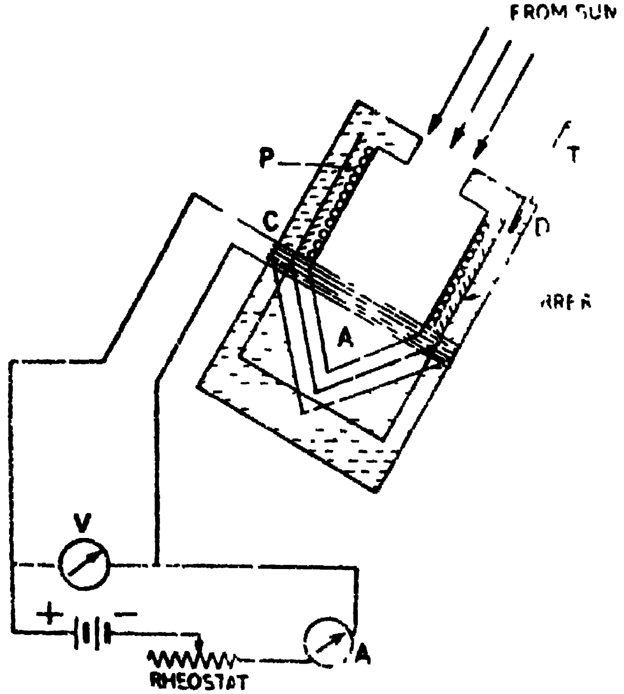


Fig. 8·[illegible]

If *E* volts is the potential difference and *I* ampere is the current passing through the manganin coil then the amount of heat produced per second $= \frac{EI}{4.2}$ cal. Therefore, the amount of heat radiations received from the sun in one minute by the exposed surface of the vessel $A = \frac{EI \times 60}{4.2}$ 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_2 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

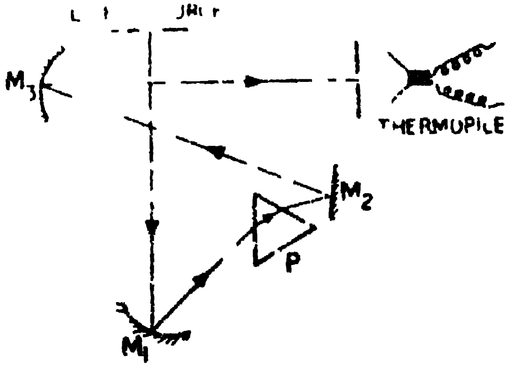


Fig. 8.52

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

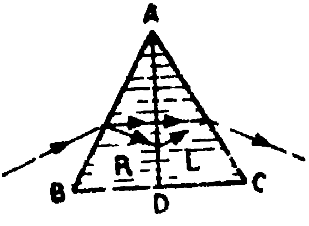


Fig. 8.53

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^{4}	
	10^{5}	10^{-3}	
	10^{6}	10^{-2}	
		10^{1}	
SHORT RADIO WAVES		1	10^{2}
		10	10^{1}
		10^{2}	1
			10
			10
RADIO BROADCAST WAVES			10
			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

(*Berhampur 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 law of heat radiation

(*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 1965*)

20 Describe Lee's method for determining the thermal conductivity of poor conductors (*Agra 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 19[illegible], Gorakhpur 1967 Delhi 1976*)

25 Give an account of any one method for measuring high temperatures by radiation pyrometers

(*Gorakhpur 1967, Delhi 19[illegible]*)

26 Describe and discuss the Ingen-Hausz method of comparing the conductivities of two metals (*Gorakhpur 19[illegible]*)

27. Describe Lee's method of 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 its 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 1975*)

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

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

(*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 [illegible]

(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 $-20°C$.

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

[**Ans.** 3 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 $-10°C$.

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

[**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.

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

[**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.

$$\sigma = 5{\cdot}672\times10^{-8} \text{ M.K.S units}$$

[**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.

$$\sigma = 5{\cdot}672\times10^{-8} \text{ M.K.S. units}$$

[**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.

$$\sigma = 5{\cdot}672\times10^{-8} \text{ M.K.S. units.}$$

[**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 $7{\cdot}65\times10^{4}$ 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

(*i*) Planck's law (*Delhi 1972*)

(*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 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 , 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

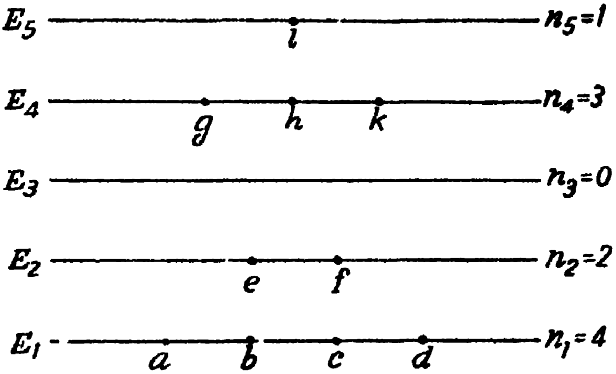


Fig. 9·1

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,

$$p_1 = \frac{N!}{n_1!(N-n_1)!} \qquad ...(i)$$

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,

$$p_2 = \frac{(N-n_1)\,!}{n_2\,!\,(N-n_1-n_2)\,!} \qquad \ldots(ii)$$

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.

$$\therefore \qquad P = p_1 \times p_2 \times p_3 \times \ldots\ldots$$

$$P = \left[\frac{N\,!}{n_1\,!\,(N-n_1)\,!}\right]\left[\frac{(N-n_1)\,!}{n_2\,!\,(N-n_1-n_2)}\right] \times \ldots\ldots$$

$$P = \frac{N\,!}{n_1\,!\,n_2\,!\,n_3\,!\ldots} \qquad \ldots(iii)$$

As shown in Fig. 9 1, the distinguishable ways are,

$$P = \frac{N\,!}{4\,!\,2\,!\,0\,!\,3\,!\,1\,!} \qquad \ldots(iv)$$

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

$$P = \frac{N\,!\,g_1^{n_1}\,g_2^{n_2}\,g_3^{n_3}\ldots\ldots\ldots}{n_1\,!\,n_2\,!\,n_3\,!\,n_4\,!\ldots\ldots\ldots} \qquad \ldots(v)$$

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_1 and particles in state E_4 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

$$P = \frac{1}{N\,!}\left[\frac{N\,!\,g_1^{n_1}\,g_2^{n_2}\,g_3^{n_3}\ldots\ldots}{n_1\,!\,n_2\,!\,n_3\,!\ldots\ldots}\right]$$

$$\therefore \qquad P = \frac{g_1^{n_1}\,g_2^{n_2}\,g_3^{n_3}\ldots\ldots}{n_1\,!\,n_2\,!\,n_3\,!}$$

$$\therefore \qquad P = \prod^{N} \frac{g_i^{n_i}}{n_i\,!} \qquad \ldots(vi)$$

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

$$\sum_i n_i = N \quad ...(vii) \quad \text{and} \quad \sum_i n_i E_i = U \quad ...(viii)$$

According to Stirling's approximation

$$\log_e x! = x \log_e x - x$$

From equation (*vi*), applying Stirling's approximation, we get

$$\begin{aligned}\log_e P &= \sum_i (n_i \log_e g_i - \log_e n_i!)\\ &= \sum_i [n_i \log_e g_i - (n_i \log_e n_i - n_i)]\\ &= \sum_i (n_i \log_e g_i - n_i \log_e n_i + n_i)\\ &= \sum_i n_i - \sum_i (n_i \log_e n_i - n_i \log_e g_i)\end{aligned}$$

$$\log_e P = N - \sum_i n_i \log_e \frac{n_i}{g_i} \quad ...(ix)$$

Differentiating equation (*ix*)

$$\begin{aligned}d(\log_e P) &= -\sum_i (dn_i) \log_e \frac{n_i}{g_i} - \sum_i n_i\, d\left(\log_e \frac{n_i}{g_i}\right)\\ &= -\sum_i dn_i \log_e \frac{n_i}{g_i} - \sum_i n_i \frac{dn_i}{n_i}\\ &= -\sum_i dn_i \log_e \frac{n_i}{g_i} - \sum_i dn_i\end{aligned}$$

But $\sum_i dn_i = 0$

$$\therefore \quad -d(\log_e P) = \sum_i \left[\log_e \left(\frac{n_i}{g_i}\right)\right] dn_i \quad ...(x)$$

To obtain the maximum value of P, $d(\log_e P) = 0$

$$\therefore \quad \sum_i \log_e \left(\frac{n_i}{g_i}\right) dn_i = 0 \quad ...(xi)$$

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

$$\log_e \frac{n_i}{g_i} + \alpha + \beta E_i = 0 \qquad \text{...(xiv)}$$

or

$$\frac{n_i}{g_i} = e^{-\alpha-\beta E_i}$$

or

$$n_i = g_i e^{-\alpha-\beta E_i} \qquad \text{...(xv)}$$

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 $\sum_i g_i e^{-\beta E_i} = Z$ ...(xvi)

Here, Z is called the partition function.

$$N = e^{-\alpha}(Z) \qquad \text{...(xvii)}$$

$$\therefore \quad e^{-\alpha} = \frac{N}{Z}$$

Substituting this value in equation (*vii*)

$$n_i = \left(\frac{N}{Z}\right)\left[g_i e^{-\beta E_i}\right] \qquad \text{...(xviii)}$$

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,

$$N = 6000,\ n_1 = 3000,\ n_2 = 2500,\ n_3 = 500$$

$$P_1 = \frac{g^N}{n_1!\, n_2!\, n_3!}$$

$$P_1 = \frac{g^{6000}}{3000!\, 2500!\, 500!} \qquad \text{...(i)}$$

In the second case

$$N = 6000$$

$$n_1 = 3001,\ n_2 = 2498,\ n_3 = 501$$

$$\therefore \quad P_2 = \frac{g^{6000}}{3001\,!\ 2498\,!\ 501\,!} \qquad \text{...(ii)}$$

Dividing (*ii*) by (*i*)

$$\frac{P_2}{P_1} = \frac{3000\,!\ 2500\,!\ 500\,!}{3001\,!\ 2498\,!\ 501\,!}$$

$$\frac{P_2}{P_1} = \frac{2500 \times 2499}{3001 \times 501} \qquad \text{...(iii)}$$

$$\frac{P_2}{P_1} = 4{\cdot}157 \qquad \text{.. (iv)}$$

$$\approx 4{\cdot}2$$

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 $e^{-\alpha} = \dfrac{N}{Z}$

$$\therefore \quad U = \frac{N}{Z}\left[g_1 E_1 e^{-\beta E_1} + g_2 E_2 e^{-\beta E_2} + \ldots\ldots\right]$$

$$U = \frac{N}{Z} \sum_i g_i E_i e^{-\beta E_i} \qquad \text{...(i)}$$

Here $Z = \sum_i g_i e^{-\beta E_i}$

$$\frac{dZ}{d\beta} = \frac{d}{d\beta} \sum_i g_i e^{-\beta E_i} = -\sum_i g_i E_i e^{-\beta E_i}$$

$$\therefore \quad \Sigma\, g_i E_i e^{-\beta E_i} = -\frac{d}{d\beta} \sum_i g_i e^{-\beta E_i}$$

Substituting this value in equation (*i*)

$$U = -\frac{N}{Z} \frac{d}{d\beta} \sum_i g_i e^{-\beta E_i}$$

$$U = -\frac{N}{Z}\frac{dZ}{d\beta}$$

$$U = -N\frac{d}{d\beta}\left[\log_e Z\right] \qquad ...(ii)$$

The average energy of a particle is

$$E_{av} = \frac{U}{N} = -\frac{d}{d\beta}\left(\log_e Z\right) \qquad ...(iii)$$

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

$$\beta = \frac{1}{kT} \quad \text{or} \quad kT = \frac{1}{\beta} \qquad ...(iv)$$

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

$$Z = \sum_i g_i\, e^{-(E_i/kT)} \qquad ...(v)$$

$$n_i = \frac{N}{Z}\, g_i\, e^{-(E_i/kT)} \qquad ...(vi)$$

This equation represents the Maxwell Boltzmann distribution law in terms of the temperature of the system

As $$\beta = \frac{1}{kT}$$

$$d\beta = -\frac{dT}{kT^2}$$

Substituting this value in equation (ii)

$$\therefore \quad U = \left(kNT^2\right)\frac{d}{dT}\left(\log_e Z\right) \qquad ...(vii)$$

Also, from equation (iii)

$$E_{av} = \left(kT^2\right)\frac{d}{dT}\left(\log_e Z\right) \qquad ...(viii)$$

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 $$g(E)\, dE = \left(\frac{4\pi V (2m^3)^{1/2}}{h^3}\right) E^{1/2}\, dE$$

Here V is the volume occupied by the gas and h is Planck's constant

$$\therefore \quad Z = \frac{4\pi V (2m^3)^{1/2}}{h^3} \int_0^\infty E^{1/2}\, e^{-E/kT}\, dE$$

$$Z = \frac{4\pi V (2m^3)^{1/2}}{h^3}\left[\frac{\sqrt{\pi}(kT)^{3/2}}{2}\right]$$

$$Z = \frac{V(2\pi m k T)^{3/2}}{h^3} \qquad \ldots(i)$$

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,

$$U = N E_{av}$$

$$U = N\left(\frac{3}{2}kT\right)$$

$$U = \frac{3}{2}NkT \qquad (ii)$$

Equation (*ii*) 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 [illegible] 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 [illegible] 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 [illegible] 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 [illegible] all the [illegible] result.

9 8 Phase Space

In [illegible] the state [illegible] non-[illegible] classical [illegible] the system. [illegible] is completely known if the position and momentum of [illegible] 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 Δx, Δy, Δz, Δp_x, Δp_y, Δp_z.

The volume of each state is given by

$$H = \Delta x \, \Delta y \, \Delta z \, \Delta p_x \, \Delta p_y \, \Delta p_z \qquad \ldots(i)$$

According to Hiesenburg's uncertainty principle,

$$\Delta x \;\; \Delta p_x \approx h$$

$$\Delta y \;\; \Delta p_y \approx h$$

$$\Delta z \;\; \Delta p_z \approx h$$

$$\therefore \quad \Delta x \, \Delta p_x \, \Delta y \, \Delta p_y \, \Delta z \, \Delta p_z = h^3 \qquad \ldots(ii)$$

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 $(2\,l + 1)$ 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

$$= g_i\,(g_i-1)\,(g_i-2)\ldots\ldots[g_i-(n_i-1)]$$

$$= \frac{g_i\,!}{(g_i-n_i)\,!} \qquad \ldots(i)$$

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,

$$= \frac{g_i\,!}{n_i\,!\,(g_i-n_i)\,!} \qquad \ldots(ii)$$

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.

$$\therefore \qquad P = \frac{g_1\,!}{n_1\,!\,(g_1-n_1)\,!}\cdot\frac{g_2\,!}{n_2\,!\,(g_2-n_2)\,!}\ldots\ldots$$

$$P = \prod_i \frac{g_i\,!}{n_i\,!\,(g_i-n_i)\,!} \qquad \ldots(iii)$$

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,

$$\log_e P = \sum_i [(g_i \log_e g_i - g_i) - (n_i \log_e n_i - n_i)$$

$$-[(g_i-n_i)\log_e (g_i-n_i) - (g_i-n_i)]]$$

$$\log_e P = \sum_i [g_i \log_e g_i - n_i \log_e n_i - (g_i-n_i) \log_e (g_i-n_i)] \qquad \ldots(iv)$$

Differentiating equation (*iv*)

$$-d\,(\log_e P) = \sum [\log_e n_i - \log_e (g_i-n_i)]\,dn_i$$

To obtain the maximum value of P,

$$d\,(\log_e P) = 0$$

$$\therefore \quad \sum_i \left[\log_e n_i - \log_e (g_i - n_i)\right] dn_i = 0 \qquad \ldots(v)$$

But $\sum_i dn_i = 0 \qquad \ldots(vi)$

and $\sum_i E_i \, dn_i = 0 \qquad \ldots(vii)$

Multiplying (*vi*) by α and (*vii*) by β and adding to equation (*v*), we get

$$\sum_i \left[\log n_i - \log_e (g_i - n_i) + \alpha + \beta E_i\right] dn_i = 0$$

The equilibrium distribution is possible if

$$\therefore \quad \log_e n_i - \log_e (g_i - n_i) + \alpha + \beta E_i = 0 \qquad \ldots(viii)$$

$$\log_e \left(\frac{n_i}{g_i - n_i}\right) = -\alpha - \beta E_i$$

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 $$n_i = \frac{g_i}{\left(e^{\alpha + \beta E_i}\right) + 1} \qquad \ldots(ix)$$

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.

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

$$\therefore \quad n_i = \frac{g_i}{\left[e^{(\alpha + E_i/kT)}\right] + 1} \qquad \ldots$$

In most cases the value of α is negative and is taken to be equal to

$$\frac{-E_F}{kT}$$

$$\therefore \quad n_i = \frac{g_i}{\left[e^{(E_i - E_F)/kT}\right] + 1} \qquad \ldots(xi)$$

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 $T \to 0$

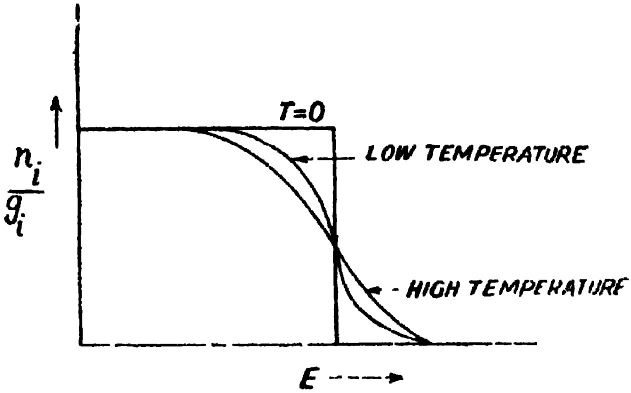


Fig. 9 2

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 ± ½, 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
$$E = \frac{p^2}{2m} = \frac{\left(\frac{h}{2\pi}\right)^2(k_F)^2}{2m}$$

∴
$$k_F = \frac{p}{h/2\pi} = \frac{2\pi p}{h}$$

∴
$$n = \frac{2\left[\frac{V}{(2\pi)^3}\right]\left[\frac{4}{3}\pi\left(\frac{2\pi p}{h}\right)^3\right]}{\left[e^{(E_i-E_F)/kT}\right]+1}$$

But $p = (2mE)^{1/2}$

∴
$$n = \frac{2\left[\frac{V}{(2\pi)^3}\right]\left[\frac{4}{3}\pi\left(\frac{2\pi}{h}\right)^3(2mE)^{3/2}\right]}{\left[e^{(E_i-E_F)/kT}\right]+1}$$

$$n = \frac{\left(\frac{8\pi V}{3h^3}\right)(2m)\,(2m)^{1/2}\,E^{3/2}}{\left[e^{(E_i-E_F)/kT}\right]+1}$$

Differentiating

$$dn = \frac{\left(\frac{8\pi V}{3h^3}\right)(2m)\,(2m)^{1/2}\times\frac{3}{2}\,E^{1/2}\,dE}{\left[e^{(E_i-E_F)/kT}\right]+1}$$

$$\frac{dn}{dE} = \frac{\left[\frac{8\pi V\,(2m^3)^{1/2}}{h^3}\right]E^{1/2}}{\left(e^{(E_i-E_F)/kT}\right)+1} \qquad \text{...}(ii)$$

Equation (ii) represents the energy distribution for free electrons. This is also called Fermi-Dirac formula of free fermions.

At $T = 0K$, ...(iii)

$p = (2m\,E_F)^{1/2}$

and $$N = \left(\frac{2V}{h^3}\right)\left(\frac{4}{3}\pi p^3\right)$$

or $$p = \left(\frac{3Nh^3}{8\pi V}\right)^{1/3} \qquad \ldots(iv)$$

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 $$E_F = \frac{h^2}{8m}\left(\frac{3N}{\pi V}\right)^{2/3} \qquad \ldots(v)$$

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 $\frac{N}{V} = 5.86 \times 10^{28}$ electrons/m³

$$\therefore \quad E_F = \left(\frac{(6.624 \times 10^{-34})^2}{8 \times 9 \times 10^{-31}}\right)\left(\frac{3 \times 5.86 \times 10^{28}}{3.14}\right)^{2/3}$$

$$E_F = 9 \times 10^{-19}\ \text{J}$$

But $1\ \text{eV} = 1.6 \times 10^{-19}\ \text{J}$

$$\therefore \quad E_F = \frac{9 \times 10^{-19}}{1.6 \times 10^{-19}}$$

$$E_F = 5.625\ \text{eV}$$

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	2.4×10^4
Sodium	3·12	3.7×10^4
Lithium	4·72	5.5×10^4
Silver	5·51	6.4×10^4
Gold	5·54	6.4×10^4
Copper	7·04	8.2×10^4

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

$$P = \frac{(n_1+g_1-1)\,!}{n_1\,!\,(g_1-1)\,!} \times \frac{(n_2+g_2-1)\,!}{n_2\,!\,(g_2-1)\,!} \times \ldots\ldots$$

$$P = \prod_i \frac{(n_i+g_i-1)\,!}{n_i\,!\,(g_i-1)\,!} \qquad \ldots(i)$$

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 $$\sum_i n_i = N \qquad \ldots(ii)$$

and $$\sum_i n_i E_i = U \qquad \ldots(iii)$$

From equation (i), applying Stirling's approximation

$$\log_e P = \sum_i \left[\log_e (n_i+g_i-1)\,! - \log_e n_i\,! - \log_e (g_i-1)\,!\right]$$

$$\log_e P = \sum_i [(n_i+g_i-1)\log_e (n_i+g_i-1) - (n_i+g_i-1)$$
$$-(n_i \log_e n_i - n_i)$$
$$-[(g_i-1)\log_e (g_i-1) - (g_i-1)]]$$

$$\log_e P = \sum_i [(n_i+g_i-1)\log_e (n_i+g_i-1)$$
$$- n_i \log_e n_i - (g_i-1)\log_e (g_i-1)] \qquad \ldots(iv)$$

The maximum value of P is obtained by taking $d\,(\log_e P) = 0$. Differentiating equation P,

$$d\,(\log_e P) = \sum_i \left[\log_e (n_i+g_i-1)\, dn_i - \log_e n_i\, dn_i\right] = 0$$

$$\therefore \qquad -d\,(\log_e P) = \sum_i\left[-\log_e (n_i+g_i-1)\, dn_i + \log_e n_i dn_i\right] = 0$$

or

$$\sum_i \left[-\log_e (n_i+g_i-1) + \log_e n_i\right] dn_i = 0 \qquad \ldots(v)$$

As the total number of particles and total energy are constants, we have,

$$\sum_i dn_i = 0 \qquad \ldots(vi)$$

$$\sum_i E_i\, dn_i = 0 \qquad \ldots(vii)$$

Multiplying equation (vi) by α and equation (vii) by β and adding to equation (v) we get,

$$\sum_i \left[-\log_e (n_i+g_i-1) + \log_e n_i + \alpha + \beta E_i\right] dn_i = 0$$

$$\therefore \qquad -\log_e (n_i+g_i-1) + \log_e n_i + \alpha + \beta E_i = 0$$

Taking n_i+g_i very large as compared to 1, the quantity 1 can be neglected.

$$\therefore \qquad -\log_e (n_i+g_i) + \log_e n_i + \alpha + \beta E_i = 0$$

$$\log_e \left(\frac{n_i}{n_i+g_i}\right) = -\alpha - \beta E_i$$

$$\frac{n_i}{n_i+g_i} = e^{-\alpha-\beta E_i}$$

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

$$n_i = \frac{g_i}{\left(e^{\alpha+\beta E_i}\right) - 1} \qquad \ldots(viii)$$

Equation ($viii$) refers to Bose-Einstein distribution law.

$$\text{Taking } \beta = \frac{1}{kT}$$

$$n_i = \frac{g_i}{\left[e^{(\alpha+E_i/kT)}\right] - 1} \qquad \ldots(ix)$$

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.

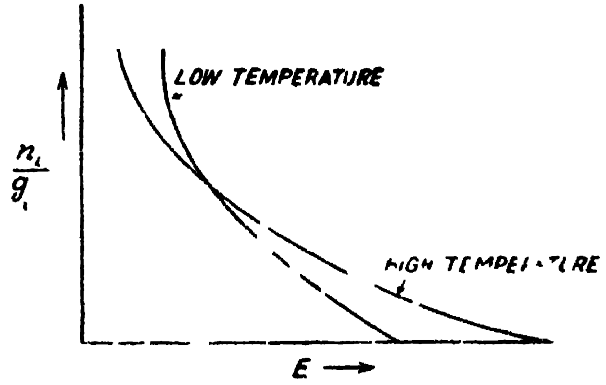


Fig 9.3

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

$$n_i = \frac{g_i}{\left(e^{(\alpha + E_i/kT)}\right) - 1} \qquad \ldots(i)$$

Here $\alpha = 0$

$$n_i = \frac{g_i}{\left(e^{E_i/kT}\right) - 1} \qquad \ldots(ii)$$

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

$$dn = \frac{g(E)\,dE}{\left(e^{E/kT}\right)-1} \qquad \text{..(iii)}$$

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 bounded by two spheres of radii $\frac{h(\nu+d\nu)}{c}$ and $\frac{h\nu}{c}$.

The volume of the spherical shell

$$\frac{4}{3}\pi\frac{h^3}{c^3}(\nu+d\nu)^3 - \frac{4}{3}\pi\frac{h^3}{c^3}\nu^3$$

$$= \frac{4}{3}\pi\frac{h^3}{c^3}\left[\nu^3 + 3\nu^2 d\nu + \ldots - \nu^3\right]$$

$$= \frac{4}{3}\pi\frac{h^3}{c^3}\times 3\nu^2 d\nu$$

$$= 4\pi\frac{h^3}{c^3}\nu^2\,d\nu \qquad \text{..(iv)}$$

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

$$g(\nu)\,d\nu = \frac{8\pi V}{c^3}\nu^2\,d\nu \qquad \text{(v)}$$

$$\therefore \quad dn = \left(\frac{8\pi V\,\nu^2 d\nu}{c^3}\right)\frac{1}{\left(e^{h\nu/kT}\right)-1} \qquad \text{(vi)}$$

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

$$= \frac{(h\nu)\,dn}{V}$$

Therefore, the energy density distribution for black body radiation is given by

$$E(\nu) = \frac{(h\nu)\,dn}{V\ d\nu} \qquad \text{...(vii)}$$

Substituting the value of dn from equation (vi), we get

$$E(\nu) = \frac{8\pi V \nu^2 d\nu \, . \, h\nu}{c^3 V \, . \, d\nu \left[\left(e^{h\nu/kT} \right) - 1 \right]}$$

$$E(\nu) = \left(\frac{8\pi h \nu^3}{c^3} \right) \left[\frac{1}{\left(e^{h\nu/kT} \right) - 1} \right] \qquad ...(vii)$$

Equation ($viii$) represents Planck's radiation law on 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 $\nu = \frac{c}{\lambda}$

$$\therefore \quad d\nu = -\frac{c}{\lambda^2} d\lambda$$

Neglecting the negative sign, we get

$$E(\lambda) \, d\lambda = \frac{8\pi h \nu^3}{c^3} \times \frac{c}{\lambda^2} \left[\frac{1}{\left(e^{h\nu/kT} \right) - 1} \right] d\lambda$$

$$\text{or} \qquad E(\lambda) = \frac{8\pi hc}{\lambda^5} \left[\frac{1}{\left(e^{h\nu/kT} \right) - 1} \right] \qquad ...(ix)$$

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 distibution
8. Applicable to ideal gas molecules	8. Applicable to electrons of high concentration.	8. Applicable to photons and symmetrical particles such as α 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 photon gas

10 From Bose Einstein statistics thermodynamics show that

$$E(\lambda) = \frac{8\pi hc}{\lambda^5}\left[\frac{1}{\left(e^{hc/\lambda kT}\right)-1}\right]$$

11 Derive Planck's radiation law for 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 $E_1 = 0$, $E_2 = \varepsilon$, $E_3 = 2\varepsilon$ All the three states have the same intrinsic 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

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad \ldots(i)$$

In the case of a surface film the corresponding TdS equation can be obtained by replacing V by A and P by $-S$

$$TdS = C_A dT - T\left(\frac{\partial S}{\partial T}\right)_A dA \qquad \ldots(ii)$$

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

$$H = -T\left(\frac{dS}{dT}\right)A \qquad \ldots(iii)$$

The work done

$$W = -S(A - 0)$$

or

$$W = -SA \qquad \ldots(iv)$$

From the first law of thermodynamics

$$H = (U - U_0) + W$$

or

$$U - U_0 = H - W \qquad \ldots(v)$$

Substituting the values of H and W

$$U-U_0 = -T\left(\frac{dS}{dT}\right)A-(-SA)$$

$$U-U_0 = \left[S-T\left(\frac{dS}{dT}\right)\right]A \qquad \ldots(vi)$$

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)

$$\left(\frac{U-U_0}{A}\right) = S-T\left(\frac{dS}{dT}\right) \qquad \ldots(vii)$$

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

$$\frac{1}{2}\,m\,C^2_{rms} = \frac{3}{2}\,kT$$

$$C^2_{rms} = \frac{3kT}{m}$$

$$C_{rms} = \sqrt{\frac{3kT}{m}} \qquad \ldots(i)$$

2 Average Velocity

$$C_{av} = \frac{\int_0^\infty C\, dN}{N}$$

But, according to Maxwell's law of distribution

$$dN = 4\pi N A^3 e^{-bC^2} C^2\, dC$$

$$\therefore \qquad C_{av} = \frac{\int_0^\infty C\, 4\pi N A^3 e^{-bC^2} C^2\, dC}{N}$$

$$= 4\pi A^3 \int_0^\infty C^3 e^{-bC^2}\, dC = (4\pi A^3)\left(\frac{1}{2b}\right)$$

$$\text{but} \qquad A = \left[\frac{m}{2\pi kT}\right]^{3/2} \text{ and } b = \frac{m}{2kT}$$

$$C_{av} = 4\pi\left[\frac{m}{2\pi kT}\right]^{3/2}\left(\frac{2kT}{m}\right)^2$$

$$C_{av} = \left[\frac{8kT}{\pi m}\right]^{1/2} \qquad (A.2)$$

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

$$\frac{d}{dC}\left[e^{-bC^2} C^2\right]_{C=C_m} = 0$$

$$-2bC_m^3 e^{-bC^2} + 2C_m e = 0$$

or

$$-bC_m^2 + 1 = 0$$

$$C_m = \left[\frac{1}{b}\right]^{1/2}$$

But $$b = \frac{m}{2kT}$$

$$C_m = \left[\frac{2kT}{m}\right]^{\frac{1}{2}} \qquad (iii)$$

∴ From equations (i) (ii) and (iii)

$$C_m : C_{av} : C_{rms} = \left[\frac{2kT}{m}\right]^{\frac{1}{2}} : \left[\frac{8kT}{\pi m}\right]^{\frac{1}{2}} : \left[\frac{3kT}{m}\right]^{\frac{1}{2}}$$

$$1 : 1.128 : 1.224$$

This relation gives the relative magnitudes of the three velocities at a given temperature. The three velocities are shown in Fig A.1

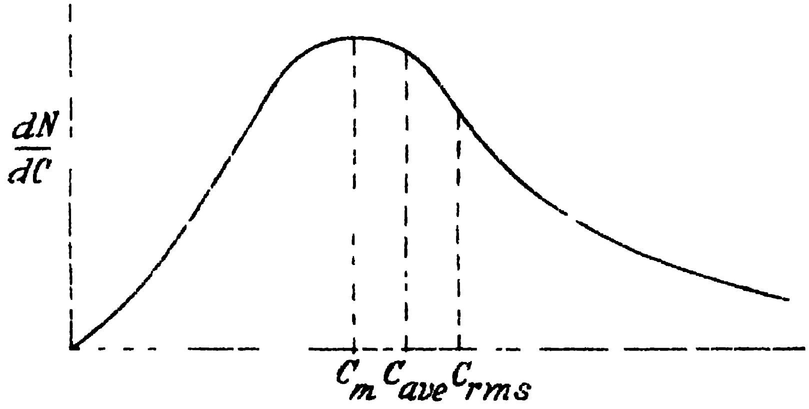


Fig. A.1

A-3 EMF of a Reversible Cell

The first TdS equation is given by

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV \qquad (i)$$

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

$$\therefore \quad TdS = C_q\,dT - T\left(\frac{\partial E}{\partial T}\right)_q dq \qquad ...(ii)$$

For a reversible cell, in which the *EMF* depends only on temperature,

$$TdS = C_q\,dT - T\left(\frac{\partial E}{\partial T}\right)_q dq \qquad ...(iii)$$

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,

$$\delta W = -E(q_f - q_i) = -E\Delta q \qquad \ldots(v)$$

Here $\Delta q = (q_f - q_i)$

$$\therefore \quad \delta H = -T\left(\frac{\partial E}{\partial T}\right)\Delta q \qquad \ldots(vi)$$

From the first law of thermodynamics

$$\delta H = dU + \delta W$$

$$\therefore \quad dU = \delta H - \delta W$$

$$dU = \Delta q\left[E - T\left(\frac{\partial E}{\partial T}\right)\right] \qquad \ldots(vii)$$

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*)

$$dh = \Delta q\left[E - T\left(\frac{\partial E}{\partial T}\right)\right] \qquad \ldots(ix)$$

dh represents the net transfer of heat between the final and the initial states of the reaction.

From equation (*ix*)

$$\frac{dh}{\Delta q} = E - T\left(\frac{\partial E}{\partial T}\right)$$

or

$$E = \left(\frac{dh}{\Delta q}\right) + T\left(\frac{\partial E}{\partial T}\right)$$

Let $\left(\frac{dh}{\Delta q}\right) = H$

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

$$=(1\times dh)\,\rho\, g=\rho\, g\, dh$$

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,

$$(P+dP)-P+(g\,\rho\,dh)=0$$

or
$$dP+g\,\rho\,dh=0$$

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

For a perfect gas

$$P=nkT,$$

and
$$dP=kT\,dn$$

and
$$\rho=mn$$

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

$$\log n=-\left(\frac{Nmg}{RT}\right)h+K \qquad (iii)$$

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)

$$\log n=-\left(\frac{Nmg}{RT}\right)h+\left(\frac{Nmg}{RT}\right)h_0+\log n_0$$

$$\log\left(\frac{n}{n_0}\right)=-\left(\frac{Nmg}{RT}\right)(h-h_0) \qquad (iv)$$

$$\therefore \quad n=n_0\left[e^{-\left(\frac{Nmg}{RT}\right)(h-h_0)}\right] \qquad (v)$$

§ A-6. Determination of Avogadro's number (N)

From equation (v)

$$N = \frac{RT \log\left(\frac{n_0}{n}\right)}{mg\,(h - h_0)} \quad \text{.. (vi)}$$

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

$$\therefore \quad N = \frac{3RT \log\left(\frac{n_0}{n}\right)}{4\pi a^3 g(d_1 - d_2)(h - h_0)} \quad \text{(vii)}$$

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

$$d_1 = \frac{m_3 d}{(m_1 + m_3 - m_2)} \quad \text{(viii)}$$

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

$$\therefore \quad 6\pi\eta a v = \frac{4}{3}\pi a^3 (d_1 - d_2) g$$

$$a = \left[\frac{9\eta v}{2(d_1 - d_2)g}\right]^{\frac{1}{2}} \quad \text{(ix)}$$

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

$$m\left(\frac{d^2x}{dt^2}\right) = -f\left(\frac{dx}{dt}\right)+F \qquad \ldots(i)$$

Here, $-f\left(\frac{dx}{dt}\right)$ represents the component of the frictional force in the x— direction. F is the combined force due to other influences. Multiply equation (*i*) by x,

$$mx\left(\frac{d^2x}{dt^2}\right) = -fx\left(\frac{dx}{dt}\right)+Fx \qquad \ldots(ii)$$

Also $$\frac{d}{dt}(x^2) = 2x\left(\frac{dx}{dt}\right) \text{ and } x\left(\frac{dx}{dt}\right) = \frac{1}{2}\frac{d}{dt}(x^2)$$

$$\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right] = 2\left[x\left(\frac{d^2x}{dt^2}\right)+\left(\frac{dx}{dt}\right)^2\right]$$

$$\therefore \quad x\left(\frac{d^2x}{dt^2}\right) = \frac{1}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]-\left(\frac{dx}{dt}\right)^2 \qquad \ldots(iii)$$

Substituting these values in equation (*ii*)

$$\frac{m}{2}\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]-m\left(\frac{dx}{dt}\right)^2 = -\frac{f}{2}\frac{d}{dt}(x^2)+Fx \qquad \ldots(iv)$$

Equation (*iv*) represents the motion of a single particle. For all the particles, the mean value can be written as

$$\frac{m}{2}\,\overline{\frac{d}{dt}\left[\frac{d}{dt}(x^2)\right]}-m\overline{\left(\frac{dx}{dt}\right)^2} = -\frac{f}{2}\,\overline{\frac{d}{dt}(x^2)}+\overline{Fx} \qquad \ldots(v)$$

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
$$\frac{dU}{dt}+\left(\frac{f}{m}\right)U = \frac{2kT}{m} \qquad \text{...}(vi)$$

The general, solution of equation (*vi*) is

$$U = \frac{2kT}{f} + A\left[e^{-\left(\frac{f}{m}\right)t}\right] \qquad \text{...}(vii)$$

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

$$\therefore \qquad u = \frac{2kT}{f} = \frac{d(\overline{x^2})}{dt} \qquad \text{...}(viii)$$

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

$$\therefore \qquad \overline{\Delta x^2} = \left(\frac{2kT}{f}\right)\tau \qquad \text{...}(ix)$$

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,

$$f\left(\frac{dx}{dt}\right) = 6\pi\eta a v = 6\pi\eta a\left(\frac{dx}{dt}\right)$$

$$\because \qquad f = 6\pi\eta a$$

$$\therefore \qquad \overline{\Delta x^2} = \frac{2kT\tau}{6\pi\eta a} = \frac{kT\tau}{3\pi\eta a} \qquad \text{...}(x)$$

or
$$\left[\overline{\Delta x^2}\right]^{\frac{1}{2}} = \frac{(kT)^{\frac{1}{2}}(\tau)^{\frac{1}{2}}}{(3\pi\eta a)^{\frac{1}{2}}} \qquad \text{...}(xi)$$

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, $$(\overline{\Delta x^2})^{\frac{1}{2}} \propto \tau^{\frac{1}{2}}$$

and $$\left(\overline{\Delta x^2}\right)^{\frac{1}{2}} \propto \frac{1}{\eta^{\frac{1}{2}}}$$

The effect of temperature is not very large because $(\overline{\Delta x^2})^{\frac{1}{2}} \propto T^{\frac{1}{2}}$ 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 Δ. 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 $T = \frac{1}{2} n_1 A \Delta$

Similarly, the number of particles crossing the surface Q in the opposite direction $= \frac{1}{2} n_2 A \Delta$

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 $= \frac{1}{2} (n_1 - n_2) A \Delta$

From the definition of diffusion coefficient, the number,

$$\frac{1}{2}(n_1 - n_2) A \Delta = -D \frac{dn}{dx} \tau A$$

Here $\left(\frac{dn}{dx}\right)$ is the concentration gradient.

But $$(n_1 - n_2) = -\Delta \frac{dn}{dx}$$

$$\therefore \quad -\frac{1}{2}\Delta^2\left(\frac{dn}{dx}\right) = -D\left(\frac{dn}{dx}\right)\tau$$

$$\therefore \qquad \Delta^2 = 2D\tau$$

or
$$D = \frac{\Delta^2}{2\tau} \qquad \ldots(i)$$

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

$$= nA\Delta$$

where n is the mean concentration.

Therefore, the force acting on a single particle

$$f' = \frac{(n_1-n_2)\,kTA}{nA\Delta} \qquad \ldots(ii)$$

Substituting the value of $(n_1-n_2) = -\Delta\dfrac{dn}{dx}$ in equation (ii)

$$f' = -\left(\frac{dn}{dx}\right)\left(\frac{kT}{n}\right)$$

$$\therefore \qquad 6\pi\eta av = -\left(\frac{kT}{n}\right)\left(\frac{dn}{dx}\right)$$

or
$$nv = -\left(\frac{kT}{6\pi\eta a}\right)\left(\frac{dn}{dx}\right) \qquad .(iii)$$

Here nv is the number of particles moving to the right per unit area per second

$$\therefore \qquad nv = -D\left(\frac{dn}{d}\right) \qquad \ldots(iv)$$

Equating (iii) and (iv)

$$-D\left(\frac{dn}{dx}\right) = -\left(\frac{kT}{6\pi\eta a}\right)\left(\frac{dn}{dx}\right)$$

or
$$D = \left(\frac{kT}{6\pi\eta a}\right) = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta a}\right) \qquad .(iv)$$

From equations (i) and (iv)

$$\frac{\Delta^2}{2\tau} = \left(\frac{RT}{N}\right)\left(\frac{1}{6\pi\eta a}\right)$$

$$\Delta^2 = \frac{RT}{N}\left(\frac{1}{3\pi\eta a}\right) \qquad \ldots(v)$$

Equations (*i*) and (*ii*) 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

$$\therefore \qquad \tfrac{1}{2}C\,\overline{\theta^2} = \tfrac{1}{2}\,kT \qquad \text{.. }(i)$$

$$\text{and} \qquad \tfrac{1}{2}\,I\,\overline{\omega^2} = \tfrac{1}{2}\,kT \qquad \text{...}(ii)$$

The root mean square angular displacement of the suspended system is given by

$$\theta_{rms} = \sqrt{\overline{\theta^2}} = \sqrt{\frac{kT}{C}} \qquad \text{.. }(iii)$$

For a fine quartz suspension fibre C is approximately equal to 10^{13} N-m/radian.

$$\text{and} \qquad k = 1\ 38\times10^{-23}$$

For a room temperature of 300 K.

$$\theta_{rms} = \sqrt{\frac{kT}{C}}$$

$$\theta_{rms} = \left[\frac{1{\cdot}38\times10^{21}\times300}{10^{13}}\right]^{\frac{1}{2}}$$

$$\theta_{rms} = 2\times10^{4} \text{ radian}$$

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

$$2\,(\theta_{rms}) = \frac{dx}{1}$$

$$dx = 4\times10^{-4}\text{ m} = 0{\cdot}4\text{ mm.}$$

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.

$[R = 8{\cdot}31 \text{ J/mole-K}]$

[I.A.S 1983]

Total random kinetic of one gram mole of oxygen,

$$U = \frac{3}{2}\,RT$$

$$U = \frac{3}{2} \times 8{\cdot}31 \times 300$$

$$U = \mathbf{3{\cdot}739 \times 10^3 \text{ J}}$$

Example A-2 . *The Van der Waals' constants a and b for 1 gram molecule of hydrogen are* $a = 0{\cdot}245$ atoms-litre²-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-cm⁴-mole⁻²

$b = 2{\cdot}67 \times 10^{-2}$ litre-mole⁻¹

$= 2{\cdot}67 \times 10^{-2} \times 10^3$ cm³ mole⁻¹

$R = 8{\cdot}31 \times 10^7$ ergs/mole-K

$$\therefore \quad T_c = \frac{8 \times 0{\cdot}245 \times 76 \times 13{\cdot}6 \times 980 \times 10^6}{27 \times 8{\cdot}31 \times 10^7 \times 2{\cdot}67 \times 10^{-2} \times 10^3}$$

$$T_c = \mathbf{33{\cdot}14 \text{ K}} = \mathbf{-239{\cdot}86^\circ\text{C}}$$

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
$$E = 5.64 \times 10^{-21}\ \text{J}$$
$$R = 8.32\ \text{J/mole—K}$$
$$T = 273\ \text{K}$$

$\therefore$
$$N = \frac{3 \times 8.32 \times 273}{2 \times 5.64 \times 10^{-21}}$$
$$N = 6.182 \times 10^{23}$$

Example A-4 *The diameter of the molecule of a gas is 2×10^{-8} cm and Boltzmann's constant is 1.38×10^{-23} J/K. Calculate the mean free path at NTP.*

[*Delhi* (*Hons*) *1984*]

Here
$$d = 2 \times 10^{-8}\ \text{cm} = 2 \times 10^{-10}\ \text{m}$$
$$k = 1.38 \times 10^{-23}\ \text{J/K}$$

Let n be the number of the molecules per cubic meter

$$PV = RT$$
$$PV = NkT$$
$$n = \left(\frac{N}{V}\right) = \frac{P}{kT}$$

At NTP

$$n = \frac{0.76 \times 13.6 \times 10^3 \times 9.8}{1.38 \times 10^{-23} \times 273}$$
$$n = 2.688 \times 10^{25}$$

Mean free path

$$\lambda = \frac{1}{\pi d^2 n} = \frac{1}{3.14 \times (2 \times 10^{-10})^2 \times 2.688 \times 10^{25}}$$
$$\lambda = 2.961 \times 10^{-}\ \text{m}$$

Example A-5 *Prove that*

$$\frac{K}{\eta\, C_v} = 1 \textit{ for a gas}$$

(*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

$$\frac{K}{\eta C_v} = 1$$

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* $= 3 \times 10^{25}$

(ii) *Diameter of oxygen molecule* $= 3.6 \times 10^{-10}$ m

(*Delhi* (*Hons*) *1984*)

Here $k = 1.38 \times 10^{-23}$

and $m = \dfrac{32}{6.023 \times 10^{26}} = 5{\cdot}31 \times 10^{26}$ kg

Average speed of oxygen molecule at 0°C (273 K)

$$v = \sqrt{\frac{8kT}{\pi m}}$$

$$v = \sqrt{\frac{8 \times 1.38 \times 10^{-23} \times 273}{3.14 \times 5.31 \times 10^{-26}}}$$

$$v = 426 \text{ m/s}$$

Also $d = 3.6 \times 10^{-10}$ m

$n = 3 \times 10^{25}$ molecules/m³

(*a*) Collision frequency (number of collisions per second)

$$= \pi d^2 v n$$

$$= 3.14\,(3.6 \times 10^{-10})^2 \times 426 \times 3 \times 10^{25}$$

$$= 5.2 \times 10^9$$

(*b*) Mean free path

$$\lambda = \frac{1}{\pi d^2 n} = \frac{1}{3.14 \times (3.6 \times 10^{-10})^2 \times 3 \times 10^{25}}$$

$$\lambda = 8.19 \times 10^{-8} \text{ m}$$

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/m³ *and atomic weight* = *63 5*

[*Delhi* (*Hons*) *1985*]

Taking one free electron per atom, 63 5 kg of copper contains 6 023 × 10²⁶ free electrons

Density of copper = 9000 kg/m³

$$V = \frac{63.5}{9000}$$

$$\frac{N}{V} = \frac{6.023 \times 10^{26} \times 9000}{63.5}$$

or $$\frac{N}{V} = 85.36 \times 10$$

$$E_F = \frac{h^2}{8m}\left[\left(\frac{3}{\pi}\right)\left(\frac{N}{V}\right)\right]^{2/3}$$

$$E_F = \left[\frac{(6.624\times10^{-34})^2}{8\times9\times10^{-31}}\right]\left[\frac{3\times85.36\times10^{27}}{3.14}\right]^{2/3}$$

$$E_F = 11.46\times10^{-19}\ \text{J}$$

$$E_F = \frac{11.46\times10^{-19}}{1.6\times10^{-19}}\ \text{eV}$$

$$E_F = 7.163\ \text{eV}$$

Pressure,

$$p = \frac{2U}{3V}$$

$$p = \frac{2N E_F}{3V}$$

$$p = \left(\frac{2}{3}\right)\left(\frac{N}{V}\right)E_F$$

$$p = \left(\frac{2}{3}\right)85.36\times10^{27}\times11.46\times10^{-19}$$

$$p = 6.5215\times10^{10}\ \text{N/m}^2$$

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

$$\gamma = \frac{\log\left(\dfrac{P_1}{P_2}\right)}{\log\left(\dfrac{V_2}{V_1}\right)}$$

$$\gamma = \frac{\log\left(\dfrac{80}{60}\right)}{\log\left(\dfrac{1190}{1000}\right)}$$

$$\gamma = \frac{0.1249}{0.0755}$$

$$\gamma = 1.787$$

Example A.9. *Calculate the work done when a g molecule of an ideal gas expands isothermally at 27°C to double original volume.* [*R* = *8·3 J/deg mole*] [*Delhi, 1*

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

$W = 8{\cdot}3\times300 \log_e 2$

$W = \mathbf{1725{\cdot}9\ J}$

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 1981)*

For an adiabatic process,

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

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

Here $\frac{P_2}{P_1} = 8$ and $T_1 = 273+27 = 300$ K

$\gamma = 1{\cdot}5$

$\therefore$ $(8)^{\gamma-1} = \left(\frac{T_2}{300}\right)^{\gamma}$

$$(8)^{0.5} = \left(\frac{T_2}{300}\right)^{1.5}$$

$$0{\cdot}5 \log 8 = 1{\cdot}5\,[\log T_2 - \log 300]$$

$$0{\cdot}5\,(0{\cdot}9031) = 1{\cdot}5 \log T_2 - 1{\cdot}5\times2{\cdot}4771$$

$$1{\cdot}5 \log T_2 = 0{\cdot}5\times0{\cdot}9031 - 1{\cdot}5\times2{\cdot}4771$$

$$1{\cdot}5 \log T_2 = 0{\cdot}4516 + 3{\cdot}7157$$

$$1{\cdot}5 \log T_2 = 4{\cdot}1673$$

$$\log T_2 = \frac{4{\cdot}1673}{1{\cdot}5}$$

$$\log T_2 = 2.7782$$

$$T_2 = \mathbf{600\ K}$$

$$T_2 = \mathbf{327\ C.}$$

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,

$$\eta = 30\% = 0.3 \quad T_2 = 300\text{ K}, \quad T_1 = ?$$

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

$$0.3 = 1 - \frac{300}{T_1}$$

$$T_1 = \mathbf{428.57\ K}$$

In the second case,

$$\eta' = 50\% = 0.5, \quad T_2 = 300\text{ K}, \quad T_1' = ?$$

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

$$0.5 = 1 - \frac{300}{T_1'}$$

$$T_1' = 600\text{ K}$$

Increase in temperature

$$= \mathbf{171.43\ K}$$

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, $\eta' = 40\% = \frac{2}{5}$

$$\frac{\eta'}{\eta} = \frac{2/5}{2/3} = \frac{3}{5} = 60\%$$

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 = 4.2 J/Calorie]

[Delhi 1981]

Here $T_1 = 627 + 273 = 900$ K

$T_2 = 27 + 273 = 300$ K

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

$\eta = 1 - \frac{300}{900}$

$\eta = \frac{2}{3}$ or 66·67%

Also $\frac{H_1}{H_2} = \frac{T_1}{T_2}$

Here $H_1 = 10^4$ Calories

∴ $H_2 = \frac{H_1 \times T_2}{T_1}$

$H_2 = \frac{10^4 \times 300}{900} = \frac{10^4}{3}$ Calories

Work done $W = H_1 - H_2$

$W = 10^4 - \left(\frac{10^4}{3}\right)$

$W = \frac{2 \times 10^4}{3}$ Calories

$W = \frac{2 \times 10^4}{3} \times 4.2$

$W = 2{\cdot}8 \times 10^4$ 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

$T_1 = 217°C = 490$ K

$T_2 = 17°C = 290$ K

Efficiency,

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

$$\eta = 1-\frac{300}{400}$$

$$\eta = 0{\cdot}25 = 25\%$$

Also $$\frac{H_1}{H_2} = \frac{T_1}{T_2} = \frac{400}{300} = \frac{4}{3}$$

$$\left(\frac{H_1}{H_2}\right)-1 = \left(\frac{4}{3}\right)-1$$

$$\frac{H_1-H_2}{H_2} = \frac{1}{3}$$

But $$W = H_1-H_2 = 10^5 \text{ J/s}$$

∴ $$\frac{10^5}{H_2} = \frac{1}{3}$$

$$H_2 = 3\times10^5 \text{ J/s}$$

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 $$H_1 = 4\times10^5 \text{ J/s}$$

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 temperature be T K°

$$m_1 s\,(T_1 - T) = m_2 s\,(T - T_2)$$

$$10\times1\times(333 - T) = 30\times1\,(T-293)$$

$$T = 303 \text{ K}^\circ$$

(*ii*) Change in entropy when the temphature of 10 g of water changs from 333 K to 303 K

$$\frac{\delta H}{T} = ms\int_{T_1}^{T}\frac{dT}{T}$$

$$= 10 \times 1 \times \log \frac{303}{333}$$

$$= 10 \times 2.3026 \times \log_{10}\left(\frac{303}{333}\right)$$

$$= -0.9443 \text{ cal/K}$$

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,

$$= \frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 30 \times 1 \log_e \frac{303}{293}$$

$$= 30 \times 2.3026 \log_{10} \frac{303}{293}$$

$$= +1.002 \text{ cal/K}$$

The total gain in entropy of the system

$$= +1.0020 - 0.9443$$

$$= 0.0577 \text{ cal/K}$$

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

$$dS = \frac{\delta H}{T} = \frac{10 \times 10^3 \times 1 \times 540}{373}$$

$$dS = 14{,}477 \text{ cal/K}$$

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

$$dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$$

$$dS = ms \times 2.3026 \log\left(\frac{T_2}{T_1}\right)$$

$$dS = 50 \times 1 \times 2{\cdot}3026 \log \left(\frac{363}{283}\right)$$

$$dS = \mathbf{12{\cdot}448\ cal/K}$$

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 = 2·93 + 3·12 + 14·47
= **20·52 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 = 0·18 and molecular weight of nitrogen is 28.*

[*Delhi, 1981*]

Specific heat of nitrogen $= \frac{C_v}{28} \quad \left(\frac{0{\cdot}18}{28}\right)$

Change in entropy $dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$

$$dS = \frac{1 \times 0{\cdot}18}{28} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$dS = \left(\frac{0{\cdot}18}{28}\right) \int_{323}^{373} \frac{dT}{T}$$

$$dS = \left(\frac{0\cdot18}{28}\right)\times 2\cdot3026 \ \log_{10}\left(\frac{373}{323}\right)$$

$$dS = \frac{0\cdot18\times2\cdot3026\times0\cdot0625}{28}$$

$$dS = 9\cdot253\times10^{-4}\ \text{cal/K}.$$

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 $dP = 135\cdot2$ atmospheres

$dP = 135\cdot2\times1\cdot013\times10^6$ dynes/cm^2

$V_2-V_1 = -0\cdot091$ cm^3

$L = 80$ cal/g

$L = 80\times4\cdot18\times10^7$ ergs/g

$T = 273$ K

$$\therefore \quad d = T\frac{(dP)\,T\,(V_2-V_1)}{L}$$

$$dT = \frac{135\cdot2\times1\cdot013\times10^6\times273\times(-0\cdot091)}{80\times4\cdot18\times10^7}$$

$dT = -1$ 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,

$$dS = ms\times2\cdot3026\ \log_{10}\left(\frac{T_2}{T_1}\right)$$

$$dS = 1\times10^3\times2\cdot3026\ \log_{10}\left(\frac{373}{273}\right)$$

$dS = 312$ 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

$$m = 0.0273 \text{ kg}$$

$$L = 80 \text{ Cal/g} = 80 \times 10^3 \text{ Cal/kg}$$

$$T = 273 \text{ K}$$

$$dS = \frac{\delta H}{T} \qquad dS = \frac{mL}{T}$$

$$dS = \frac{0.0273 \times 80 \times 10^3}{273}$$

$$dS = 8 \text{ Cal/K} \qquad dS = 8 \times 4.2 = \mathbf{33.6 \ J/K.}$$

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*

$$a = 13.2 \times 10^{-2} \text{ Nm}^4 \text{ (mole)}^{-2}$$

$$b = 31.2 \times 10^{-6} \text{ m}^3 \text{ (mole)}^{-1}$$

$$R = 8.3 \text{ JK}^{-1} \text{ (mole)}^{-1}$$

$$C_p = 3.5 R$$

[*Delhi (Hons) 1982*]

$$\delta T = \left(\frac{\delta P}{JMC_p}\right)\left(\frac{2a}{RT} - b\right)$$

Here δP = 50 atmorpheres

$$= 50 \times 0.76 \times 13.6 \times 10^3 \times 9.8 \text{ N/m}^2$$

$$J = 4.2 \text{ J/cal}$$

$$M = 32$$

$$C_p = 3.5R = 3.5 \times 8.3 \text{ JK}^{-1} \text{ (mole)}^{-1}$$

$$T = 300 \text{ K}$$

$$\delta T = \left(\frac{50 \times 0.76 \times 13.6 \times 10^3 \times 9.8}{4.2 \times 32 \times 3.5 \times 8.3}\right)\left(\frac{2 \times 13.2 \times 10^{-2}}{8.3 \times 300} - 31.2 \times 10^{-6}\right)$$

$$\delta T = \mathbf{0.0969 \ K}$$

Example A-25 *For a metallic copper disc at 300* K, *the following values are known*

$$C_P = 24.5 \text{ J/mol K}$$

$$\alpha = 50.4 \times 10^{-6} \text{ K}^{-1}$$

Isothermal compressibility $K = 7.78 \times 10^{-12} \text{ N}^{-1} \text{ m}^2$

$$V = 7.06 \text{ cm}^3\text{/mol}$$

Determine C_V

$$C_P - C_V = TE\alpha^2 V$$

and

$$E = \frac{1}{K}$$

$$C_P - C_V = \frac{TV\alpha^2}{K}$$

$$V = 7.06 \text{ cm}^3\text{/mol} = 7.06 \times 10^{-6} \text{ m}^3\text{/mol}$$

$$C_P - C_V = \frac{300 \times 7.06 \times 10^{-6} \times (50.4 \times 10^{-6})^2}{7.78 \times 10^{-12}}$$

$$C_P - C_V = 0.6915 \text{ J/mol-K}$$

$$C_V = C_P - 0{\cdot}6915$$

$$C_V = 24{\cdot}5 - 0{\cdot}6915$$

$$C_V = 23{\cdot}8085 \text{ J/mol-K}$$

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

$$C_p = 7 \text{ cal/mole-K}$$

(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

$$T = 273 \text{ K}, \quad V = 1{\cdot}47 \times 10^{-5} \text{ m}^3\text{/mol}$$

$$\beta = 1{\cdot}81 \times 10^{-6} \text{ K}^{-1}$$

$$k = 3{\cdot}89 \times 10^{-11} \, Pa^{-1}$$

$$\therefore \quad \frac{TV\beta^2}{k} = \frac{273 \times 1{\cdot}47 \times 10^{-5} \times (1{\cdot}81 \times 10^{-6})}{3{\cdot}89 \times 10^{-11}}$$

$$= 338 \times 10^{-6}$$

$$\therefore \quad C_V = C_P - 338 \times 10^{-6} = 28 - 338 \times 10^{-6}$$

$$= 27.999662 \text{ J/mol K}$$

$$\gamma = \frac{C_P}{C_V} = \frac{28}{27.999662} = 1$$

Example A-28 *Calculate the radius of an oxygen molecule if its coefficient of thermal conductivity*

$$K = 24\times10^{-3} \text{ J/m s-K at } 0^\circ C$$

and
$$C_v = 20{\cdot}9\times10^{3} \text{ J/kilo-mole K}$$

Boltzmann's constant $k = 1{\cdot}38\times10^{-23}$ J/K
and mass of an oxygen molecule

$$m = 5{\cdot}31\times10^{-26} \text{ kg}$$

(Rajasthan, 1981)

$$K = \frac{m\bar{C}\,C_v}{3(\sqrt{2})\pi\sigma^2}$$

But $\frac{1}{2}mC^2 = \frac{3}{2}kT$ or $C = \sqrt{\frac{3kT}{m}}$

$$\sigma^2 = \frac{mC\,C_v}{3\times1{\cdot}414\times3{\cdot}142\times K}$$

$$\sigma^2 = \frac{(\sqrt{3kT\,m})\,C_v}{3\times1{\cdot}414\times3{\cdot}142\times K}$$

$$\sigma^2 = \frac{[3\times1{\cdot}38\times10^{-23}\times273\times5{\cdot}31\times10^{-26}]^{1/2}\times20{\cdot}9\times10^{3}}{3\times1{\cdot}414\times3{\cdot}142\times24\times10^{-3}}$$

or $\sigma = 3{\cdot}036\times10^{-11}$ m

Example A-29 *If Wien's constant b = 0·3 cm K°, calculate the temperature of the sun whose radiation has maximum energy at wavelength λ = 5500 Å* *(Rajasthan, 1981)*

According to Wien's displacement law

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

$$T = \frac{b}{\lambda_m}$$

Here
$$b = 0{\cdot}3 \text{ cm K}$$

$$\lambda_m = 5500 \text{ Å} = 5500\times10^{-8} \text{ cm}$$

$$\therefore \quad T = \frac{0{\cdot}3}{5500\times10^{-8}}$$

$$T = 5455 \text{ K}$$

Example. A-30 *Deduce the temperature at which a black body loses thermal energy at the rate of 1* watt/cm²

(Rajasthan, 1981)

$$R = 1 \text{ watt/cm}^2 = 10^4 \text{ watts/m}^2$$

$$R = \sigma T^4$$

$$T^4 = \left(\frac{R}{\sigma}\right)$$

$$T = \left(\frac{R}{\sigma}\right)^{1/4}$$

$$T = \left[\frac{10^4}{5.672 \times 10^{-8}}\right]^{1/4}$$

$$T = 648 \text{ K.}$$

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 1·4 × 10^{-6}* m *with maximum energy*
[*Delhi* (*Hons*) *1983*]

According to Wien's displacement law

$$\lambda_m T' = \text{constant}$$

$$\lambda_m T = \lambda_m' T'$$

$$T' = \frac{\lambda_m T}{\lambda_m'} = \frac{4700 \times 10^{-10} \times 6174}{1.4 \times 10^{-6}}$$

$$T' = 207.27 \text{ K}$$

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 3·95 × 10^{26}* J *Also show that the rate at which energy is reaching the top of earth's atmosphere is 1·4* kW-m^{-2}
[*Delhi* (*Hons*) *1981*]

Here radius of the sun, $r = 7 \times 10^8$ m

Surface area of the sun $A = 4\pi r^2$

$$= 4 \times 3.142 \times (7 \times 10^8)^2 \text{ m}^2$$

$$\sigma = 5.672 \times 10^{-8} \; SI \text{ units}$$

$$T = 5800 \text{ K}$$

Total energy emitted by Sun per second

$$U = A \sigma T^4$$

$$U = 4 \times 3.142 \times (7 \times 10^8)^2 \times 5.672 \times 10^{-8} \times (5800)^4$$

$$U = 3.95 \times 10^{26} \text{ J}$$

Distance of the earth's atmosphere from the Sun

$$= r_1 = 1.5 \times 10^{11} \text{ m}$$

Energy reaching per unit area per second,

$$R = \frac{U}{4\pi r_1^2}$$

$$R = \frac{3.95 \times 10^{26}}{4 \times 3.142 \times (1.5 \times 10^{11})^2}$$

$$R = 1.3968 \times 10^3 \quad \text{W/m}^2$$

$$R = 1.3968 \text{ kW/m}^2$$

or $$R \approx 1.4 \text{ kW/m}^2$$

Example A-33. *Calculate the energy of 5 gram molecules of ozone (O_3) at 27°C. Given $R = 8{\cdot}3\ J/g\text{-mole}/°K$*

[Lucknow, 1990]

Here

$$U = n\left[\frac{3}{2}RT\right]$$

$$n = 5$$

$$R = 8{\cdot}3\ \text{J}/g\text{-mole}/°\text{K}$$

$$T = 27 + 273 = 300\ \text{K}$$

$$U = 5\times\left(\frac{3}{2}\right)\times 8{\cdot}3\times 300$$

$$U = \mathbf{1{\cdot}8675\times 10^4}\ \text{J}$$

Example A-34. *Calculate the pressure required to lower the melting point of ice by 1°C. Given*

L = 79·6 cal/g. Specific volumes of water at 0°C = 1 cm³.

Specific volume of ice, at 0°C = 1·091 cm³. 1 atmospheric pressure = $1{\cdot}013\times 10^6$ dyne/cm². *[Delhi 1990]*

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dT = -1\ \text{K}$$

$$T = 273\ \text{K}$$

$$V_2 - V_1 = -0{\cdot}091\ \text{cm}^3$$

$$L = 79{\cdot}6\ \text{cal}/g$$

$$79{\cdot}6\times 4{\cdot}18\times 10^7\ \text{ergs}/g$$

$$dP = \frac{L\,dT}{T\,[V_2-V_1]} = \frac{79{\cdot}6\times 4{\cdot}18\times 10^7\times 1}{273\times 0{\cdot}091}\ \text{dynes/cm}^2$$

$$dP = 1{\cdot}33932\times 10^8\ \text{dynes/cm}^2$$

$$dP = \frac{1{\cdot}33932\times 10^8}{1{\cdot}013\times 10^6}\ \text{atmospheres}$$

$$dP = \mathbf{132{\cdot}21}\ \text{atmospheres}$$

∴ Pressure required = 132·21 + 1 = **133·21 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, $T_1 = 273 + 127 = 400\ \text{K}$

$$T_2 = 273+27 = 300 \text{ K}$$

$$\sigma = 5{\cdot}672 \times 10^{-8} \text{ SI units}$$

$$R = \sigma[T_1^4 - T_2^4]$$

$$R = 5672 \times 10^{-8} [(400)^4 - (300)^4]$$

$$R = \mathbf{992{\cdot}6 \text{ watts/m}^2}$$

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 increased?* [*Delhi 1990*]

Here $T_2 = 273+7 = 280$ 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,

$$= 933{,}3 - 560 = \mathbf{373{\cdot}3 \text{ K} = 373{\cdot}3° \text{ C}}$$

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 1·4×10⁻⁵ cm with maximum energy.* [*Delhi (Hons.) 1990*]

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

$\therefore$ $\lambda_1 T_1 = \lambda_2 T_2$

$$T_1 = 6174 \text{ K}$$

$$\lambda_1 = 4700 \text{ Å}$$

$$\lambda = 1{\cdot}4 \times 10^{-5} \text{ cm} = 1400 \text{ Å}$$

$$T_2 = ?$$

$$T_2 = \frac{\lambda_1 T_1}{\lambda_2} = \frac{4700 \times 6174}{1400} = \mathbf{20727 \text{ K}}.$$

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/m^3, the Boltzmann constant $k = 1{\cdot}38\times10^{-23}$ J/K. $h = 6{\cdot}62\times10^{-34}$ J-s and $m_e = 9{\cdot}1\times10^{-31}$ 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

$$h = 6{\cdot}62\times10^{-24}\ \text{J.s}$$

$$m \quad 9{\cdot}1\times10^{-31}\ \text{kg}$$

$$\frac{N}{V} = 8{\cdot}5\times10^{28}\ \text{electrons/m}^3$$

$$\therefore \quad E_F = \left[\frac{(6{\cdot}62\times10^{-34})^2}{8\times9{\cdot}1\times10^{-31}}\right]\left[\frac{3\times85\times10^{28}}{3{\cdot}14}\right]^{2/3}$$

$$E_F = 11{\cdot}46\times10^{-19}\ \text{J}$$

$$E_F = \left(\frac{11{\cdot}46\times10^{-19}}{1{\cdot}6\times10^{-19}}\right)\text{eV} = 7{\cdot}163\ \text{eV}$$

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

$$T_1 = 100°\text{C} = 373\ \text{K}$$

$$T_2 = 0°\text{C} = 273\ \text{K}$$

$$\frac{H_1 - H_2}{H_2} = \frac{T - T_2}{T_1}$$

$$\frac{W}{H_1} = \frac{T_1 - T_2}{T_1} \qquad \text{...(i)}$$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \qquad \text{...(ii)}$$

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

$$H_2 = mL$$

$$m = \frac{H_2}{L} = \frac{16380}{80\times10^3\times4{\cdot}2} = 0{\cdot}04875\ \text{kg}$$

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 $C_1 = 1{\cdot}84 \text{ km/s}$

$$C_2 = ?$$

$$\frac{\rho_1}{\rho_2} = \frac{2}{32} = \frac{1}{16}$$

$$\frac{C_2}{C_1} = \sqrt{\frac{\rho_1}{\rho_2}}$$

$$\frac{C_2}{1{\cdot}84} = \sqrt{\frac{1}{16}}$$

$$C_2 = \frac{1{\cdot}84}{4}$$

$$C_2 = 0{\cdot}46 \text{ km/s} = \mathbf{460 \text{ m/s}}$$

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 = 4·2×10⁷ ergs/cal*] [*Delhi (Hons) 1991*]

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 787 - 760 = 27 \text{ mm of Hg}$$

$$= 2{\cdot}7 \text{ cm of Hg}$$

$$= 2{\cdot}7 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$dT = 1°\text{C} = 1 \text{ K}$$

$$T = 373 \text{ K}$$

$$V_2 - V_1 = 1601 - 1 = 1600 \text{ cm}^3$$

$$L = ?$$

$$L = \frac{T\,dP\,(V_2 - V_1)}{dT}$$

$$= \frac{373 \times 2{\cdot}7 \times 13{\cdot}6 \times 980 \times 1600}{1} \text{ ergs/g}$$

$$= \mathbf{2147{\cdot}6 \times 10^7} \text{ ergs/g}$$

$$L = \frac{2147{\cdot}6 \times 10^7}{4{\cdot}2 \times 10^7} = \mathbf{511{\cdot}33 \text{ cal/g}}$$

Example A-42. *Calculate the Fermi energy and the pressure of electrons in aluminium at absolute zero.*

Density of Al = 2·7×10³ kg/m³

Atomic weight of Al = 27 kg/k mole

$m_e = 9{\cdot}11 \times 10^{-31}$ *kg*

$h = 6{\cdot}63 \times 10^{-34}$ *J s*

[*Delhi (Hons) 1991*]

Taking one free electron per atom, 27 kg of *Al* contains $6{\cdot}023 \times 10^{26}$ free electrons.

Density of copper $= 7{\cdot}7 \times 10^{3}$ kg/m^3

$$V = \frac{27}{7{\cdot}7 \times 10^{3}}$$

$$\therefore \quad \frac{N}{V} = \frac{6{\cdot}023 \times 10^{26} \times 7{\cdot}7 \times 10^{3}}{27} = 1{\cdot}7177 \times 10^{29}$$

$$E_F = \frac{h^2}{8m}\left[\left(\frac{3}{\pi}\right)\left(\frac{N}{V}\right)\right]^{2/3}$$

$$E_F = \left[\frac{(6{\cdot}63 \times 10^{-34})^2}{8 \times 9{\cdot}11 \times 10^{-31}}\right]\left[\frac{3 \times 1{\cdot}7177 \times 10^{29}}{3{\cdot}14}\right]^{2/3}$$

$$E_F = 18{\cdot}1 \times 10^{-19}\ \mathrm{J}$$

$$E_F = \frac{18{\cdot}1 \times 10^{-19}}{1{\cdot}6 \times 10^{-19}}$$

$$E_F = 11{\cdot}31\ \mathrm{eV}$$

Pressure,
$$p = \frac{2U}{3V} = \frac{2NE_F}{3V} = \left(\frac{2}{3}\right)\left(\frac{N}{V}\right)E_F$$

$$p = \frac{2}{3} \times 171{\cdot}77 \times 10^{27} \times 18{\cdot}1 \times 10^{-19}$$

$$p = 20{\cdot}73 \times 10^{10}\ \mathrm{N/m^2}$$

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*

$$\sigma = 5{\cdot}67 \times 10^{-8}\ W/m^2\text{-}k^4$$

Here
$$e = 0{\cdot}9$$

$$A = 3\ m^2$$

$$\sigma = 5{\cdot}67 \times 10^{-8}\ W/m^2\text{-}k^4$$

$$\theta_1 = 273 + 37 = 310\ \mathrm{K}$$

$$\theta_2 = 273 + 20 = 293\ \mathrm{K}$$

$$R = eA\,\sigma\,(\theta_1^4 - \theta_2^4)$$

$$R = 0{\cdot}9 \times 3 \times 5{\cdot}67 \times 10^{-8}\,[(310)^4 - (293)^4]$$

$$R = 286\ \mathrm{J/s}$$

$$t = 10\ \text{minutes} = 600\ \mathrm{s}$$

Total heat lost by the skin in 10 minutes.

$$Q = Rt = 286 \times 600 = 1{\cdot}716 \times 10^{5}\ \mathrm{J}$$

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} m^3 to a volume 6×10^{-5} m^3. 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

$V_1 = 8\times10^{-4}\ \text{m}^3$

$V_2 = 6\times10^{-5}\ \text{m}^3$

$T_1 = 273+20 = 293\ \text{K}$

$$P_2 = 1\left[\frac{8\times10^{-4}}{6\times10^{-5}}\right]^{1\cdot4}$$

$P_2 = 37{\cdot}6$ atmospheres

(b) Since $\frac{PV}{T}$ is always constant during the process as no gas has escaped from the cylinder

$$\frac{PV}{T} = nR = \text{constant}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$T_2 = \left(\frac{P_2}{P_1}\right)\left(\frac{V_2}{V_1}\right)T_1$$

$$T_2 = \left(\frac{37{\cdot}6}{1}\right)\left(\frac{6\times10^{-5}}{8\times10^{-4}}\right)293$$

$T_2 = 826{\cdot}2\ \text{K}$

$T_2 = 553{\cdot}2°\text{C}$

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 ....*

[*I. I. T. Entrance Exam, 1991*]

Here $$\frac{dQ}{dt} = P = KA\left(\frac{dT}{dr}\right)$$

$$\frac{dQ}{dt} = K\,(4\pi r^2)\,\frac{dT}{dr} = P$$

$$\frac{dr}{r^2} = \left(\frac{4\pi K}{P}\right)dT$$

Integrating

$$\int_{r_1}^{r_2}\frac{dr}{r^2} = \frac{4\pi K}{P}\int dT$$

$$\frac{1}{r_1}-\frac{1}{r_2} = \frac{4\pi KT}{P}$$

$$(r_2 - r_1) = \left(\frac{4\pi KT}{P}\right) r_1 r_2$$

Approximately $r_1 \simeq r_2 \sim R$, $\because$ $r_1 r_2 = R^2$

$$(r_2 - r_1) = \left(\frac{4\pi KT}{P}\right) R^2$$

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 0K. 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

$$\int dt = \left(\frac{\frac{4}{3}\pi r^3\rho}{4\pi r^2}\right)\left(\frac{C}{\sigma}\right)\int_{200}^{100}\frac{dT}{T^4}$$

$$t = \left(\frac{r\rho C}{3\sigma}\right)\left(\frac{1}{3}\right)\left[\left(\frac{1}{200}\right)^3 - \left(\frac{1}{100}\right)^3\right]$$

$$t = \left[\frac{7 r\rho C}{(72\times 10^6)\sigma}\right]$$

Example A-47. *The molecular diameter of an ideal gas is 2×10^{-10} m at a temperature of 20°C and pressure 1 atmosphere. Calculate the*

(*a*) *mean free path*

(*b*) *collision frequency*

Velocity of molecules at

20°C = 511 m/s,

Take 1 atmospheric pressure

$$= 1{\cdot}01\times 10^5\ N/m^2$$

(*a*) **Here** $T = 293$ K

As the gas is ideal, the equation

$$PV = NkT \text{ can be applied}$$

$$\therefore \quad n = \frac{N}{V} = \frac{P}{kT} = \frac{1.01 \times 10^5}{(1.38 \times 10^{-23}) \times 293}$$

$$= 2.5 \times 10^{25} \text{ molecules/m}^3$$

mean free path

$$\lambda = \frac{1}{1.414\ \pi d^2 n}$$

$$\lambda = \frac{1}{1.414 \times \pi (2 \times 10^{-10})^2 \times (2.5 \times 10^{25})}$$

$$\lambda = 2.25 \times 10^{-7}\ \text{m}$$

(*b*) collision frequency

$$f = \frac{\bar{c}}{\lambda} = \frac{511}{2.25 \times 10^{-7}}$$

$$f = 2.27 \times 10^9 \text{ per second}$$

Example A 48 *Calculate the number of collisions per second of a molecule of a gas having mean free path 1.876 × 10⁻⁷ m. Take average speed of the molecule as 511 m/s.* [*Delhi, 1992*]

Mean free path $\lambda = 1.876 \times 10^{-7}$ m

$\bar{c} = 511$ m/s

Collision frequency,

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

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 = 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

$$dS = \frac{\delta H}{T} = \frac{80}{273} = 0.293 \text{ k cal/K}$$

(2) Increase in entropy when the temperature of 1 kg of water is raised from 0°C to 100°C

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T} = m \times 2.3026 \log_{10}\left(\frac{T_2}{T_1}\right)$$

$$= 1 \times 1 \times 2.3026 \log_{10}\left(\frac{373}{273}\right) = 0.312 \text{ k cal/K}$$

(3) Increase in entropy when 1 kg of water at 100°C is converted into steam at 100°C

$$dS = \frac{\delta H}{T} = \frac{540}{373} = 1.447 \text{ k cal/K}$$

Total increase in entropy,

$$dS = 0.293 + 0.312 + 1.447 = \mathbf{2.052\ k\ cal/K}$$

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

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

Here $P_2 = 2P_1$

$T_1 = 27\ ^\circ C = 27 + 273\ K$

$= 300\ K$

$T_2 = ?$

$\gamma = 1.4$

$$(2)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

$0.4 \log 2 = 1.4\ [\log T_2 - \log 300]$

$0.4 \times 0.3010 = 1.4\ [\log T_2 - 2.4771]$

$\log T_2 = 0.086 + 2.4771$

$= 2.5631$

$T_2 = 365.7\ K$

$= 365.7 - 273 = 92.7\ ^\circ C$

Rise in temperature $= (92.7 - 27)\ ^\circ C$

$= \mathbf{65.7\ ^\circ C}$

Example A-51 *Calculate the work done when one litre of a mono tomic perfect gas at N.T.P. is compressed adiabatically to half its volun* $\gamma = 1.67$

[Calicut 1992

Here $V_1 = 1$ litre $= 10^3\ cm^3 = 10^{-3}\ m^3$

$V_2 = 0.5$ litre $= 500\ cm^3 = 5 \times 10^{-4}\ m^3$

$\gamma = 1.67$

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.

$$\eta_1 = 1 - \left(\frac{H_2}{H_1}\right)$$

$$\eta_2 \quad 1 - \left(\frac{H_3}{H_2}\right)$$

$$\eta_1 = \eta_2$$

$$1 - \left(\frac{H_2}{H_1}\right) - 1 - \left(\frac{H_3}{H_2}\right)$$

$$1 - \left(-\frac{T}{1200}\right) \quad 1 - \left(\frac{300}{T}\right)$$

$$\frac{T}{1200} \quad \frac{300}{T}$$

$$T \quad \mathbf{600\ K}$$

Example A 53 *A Carnot engine working between a source at tempera ture 27 C and a sink at −73 C delivers 300 calories of heat to the latter one cycle Calculate the work performed in joules by the engine per cycle*
[Calcutta 199

Here $T \quad 27 + 273 \quad 300\ K$

$T \quad -73 + 273 \quad 200\ K$

$H \quad 300$ calories

H

$$\frac{H}{H} \quad \frac{T_1}{T_2}$$

$$\frac{H_1}{300} \quad \frac{300}{200}$$

$H \quad 450$ calories

Work performed per cycle

$W \quad H_1 - H$

$450 - 300$

150 calori

$150 \times 4\ 2$ J

630 J

Example A-54 *In a cold storage ice melts at the rate of 3 kg per h when the external temperature is 28 C Find the minimum power output 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 19

$$m = 3 \text{ kg}$$

$$L = 3.3 \times 10^{5}\ \text{J kg}^{-1}$$

$$s = 4.2 \times 10^{3} = \text{J kg}^{-1} - {^\circ}\text{C}$$

Heat taken by ice to melt into water and reach a temperature of28 °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 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* $1.090 \times 10^{-3}\ \text{m}^3$ *and* $10^{-3}\ \text{m}^3$ *respectively*

[*Kerala, 1992*]

Here, $L = 3.35 \times 10^{5}\ \text{J kg}$

$$T = 273 \text{ K}$$

$$V_1 = 1.090 \times 10^{-3}\ \text{m}^3$$

$$V_2 = 10^{-3}\ \text{m}^3$$

$$dP = 1 \text{ atmosphere}$$

$$= 0.76 \times 13.6 \times 10^{3} \times 9.8$$

$$= 1.01 \times 10^{5}\ \text{N m}^{-2}$$

$$\frac{dP}{dT} = \frac{L}{T[V_2 - V_1]}$$

$$dT = \frac{dP \times T[V_2 - V_1]}{L}$$

$$= \frac{1.01 \times 10^{5} \times 273\,[10^{-3} - 1.09 \times 10^{-3}]}{3.35 \times 10^{5}}$$

$$= -7.4 \times 10^{-3}\ \text{K}$$

$$= 7.4 \times 10^{-3}\ {^\circ}\text{C}$$

Therefore decrease in melting point of ice with an increase in pressure of one atmosphere

$$= 7.4 \times 10^{-3}\ \text{K} = 7.4 \times 10^{-3}\ ^\circ\text{C}$$

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 $dP = 100\ \text{cm Hg} = 1\ \text{m Hg}$

$$= 1 \times 13.6 \times 10^3 \times 9.8\ \text{N/m}^2$$

$$= 1.33 \times 10^5\ \text{N/m}^2$$

$$V_1 = 1\ \text{cm}^3/\text{gram} = 10^{-3}\ \text{m}^3/\text{kg}$$

$$V_2 = 1601\ \text{cm}^3/\text{gram} = 1601 \times 10^{-3}\ \text{m}^3/\text{kg}$$

$$L = 536\ \text{cal/gram}$$

$$= 536 \times 4.2 \times 10^3\ \text{J/kg}$$

$$= 2.25 \times 10^6\ \text{J/kg}$$

$$T = 100\ ^\circ\text{C} = 373\ \text{K}$$

$$dT = ?$$

$$\frac{dP}{dT} = \frac{L}{T\,[V_2 - V_1]}$$

$$dT = \frac{dP \times T\,[V_2 - V_1]}{L}$$

$$= \frac{1.33 \times 10^5 \times 373\,[1601 \times 10^{-3} - 10^{-3}]}{2.25 \times 10^6}$$

$$= \mathbf{35.28\ K}$$

$$= \mathbf{35.28\ ^\circ C}$$

Therefore, increase in boiling point of water with an increase of 100 cm in mercury pressure

$$= \mathbf{35.28\ K} = \mathbf{35.28\ ^\circ C}$$

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],

$$dP = 0.76 \times 13.6 \times 10^3 \times 9.8 = 1.01 \times 10^5\ \text{N/m}^2$$

$$L = 80 \text{ cal/gram}$$

$$= 80 \times 4.2 \times 10^{3} \text{ J/kg}$$

$$= 3.36 \times 10^{5} \text{ J/kg}$$

$$T = 273 \text{ K}$$

$$V_2 - V_1 = -0.1 \text{ cm}^3\text{/gram}$$

$$= -0.1 \times 10^{-3} \text{ m}^3\text{/kg}$$

$$dT = ?$$

$$\frac{dP}{dT} = \frac{L}{T[V_2 - V_1]}$$

$$dT = \frac{dP \times T[V_2 - V_1]}{L}$$

$$= \frac{1.01 \times 10^{5} \times 273 [-0.1 \times 10^{-3}]}{3.36 \times 10^{5}}$$

$$= -8.2 \times 10^{-3} \text{ K}$$

$$= -8.2 \times 10^{-3} \text{ °C}$$

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,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

$$= \frac{5 \times 10^5 \times 50}{2 \times 10^5 \times 20}$$

$$= 6.25$$

Also, $\frac{V_2}{V_1} = \frac{50}{25} = 2.5$

$$C_v = 21 \text{ J/mol} - \text{K}$$

$$R = 8.4 \text{ J/mol} - \text{K}$$

The change in entropy,

$$dS = C_v \times 2.3026 \log_{10}\left(\frac{T_2}{T_1}\right) + R \times 2.3026 \log_{10}\left(\frac{V_2}{V_1}\right)$$

$$= 21 \times 2.3026 \log_{10}(6.25) + 8.4 \times 2.3026 \log_{10}(2.5)$$

$$= 21 \times 2.3026 \times 0.7959 + 8.4 \times 2.3026 \times 0.3979$$

$$= 38.4852 + 7.6961$$

$$= 46.1813$$

$$= \mathbf{46.18 \text{ J/K}}$$

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

$$s = 1 \text{ kcal/kg} - {}^\circ\text{C}$$

$$= 4.2 \times 10^3 \text{ J/kg} - {}^\circ\text{C}$$

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

$$m_1 \times s \times [T - T_1] = m_2 \times s \times [T_2 - T]$$

$$m_1 [T - T_1] = m_2 [T_2 - T]$$

$$0.1 [T - 288] = 0.16 [313 - T]$$

$$T = \mathbf{303.4 \text{ K}}$$

(i) Change in entropy when the temperature of 0.1 kg of water rises from 288 K to 303.4 K

$$\frac{\delta H}{T} = ms \int_{T}^{T} \left(\frac{dT}{T} \right)$$

$$= 0.1 \times 4.2 \times 10^3 \times 2.3026 \log_{10} \left(\frac{303.4}{288} \right)$$

$$= \mathbf{21.88\ J/K}$$

(ii) Change in entropy when the temperature of 0.16 kg of water decreases from 313 K to 303.4 K

$$\frac{\delta H}{T} = ms \int_{T}^{T} \left(\frac{dT}{T} \right)$$

$$= 0.16 \times 4.2 \times 10^3 \times 2.3026 \log_{10} \left(\frac{303.4}{313} \right)$$

$$= -20.93\ J/K$$

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 = 536 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

= 3.36×10^5 J/kg

Latent heat of steam = 536 cal/gram = $536 \times 10^3 \times 4.2$ J/kg

= 2.25×10^6 J/kg

Specific heat of ice = 0.5 cal/gram − K

= $0.5 \times 10^3 \times 4.2$ J/kg − K

= 2.1×10^3 J/kg − K

Specific heat water = 1 cal/gram - K

$$= 1 \times 10^3 \; 4.2 \times \mathrm{J/kg-K}$$

$$4.2 \times 10^3 \; \mathrm{J/kg-K}$$

(1) Increase in entropy when temperature of 12.5 × 10 kg of ice is increased from −24 C to 0 C (249 K to 273 K)

$$\Delta S = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= ms \log_e \left(\frac{T_2}{T_1} \right)$$

$$= 12.5 \times 10^{-3} \times 2.1 \times 10^3 \log_e \left(\frac{273}{249} \right)$$

$$= 12.5 \times 2.1 \times 2.3026 \log_{10} \left(\frac{273}{249} \right)$$

$$= \mathbf{2.42 \; J/K}$$

(2) Increase in entropy when 12.5 × 10 kg of ice at 0 C is converted into water at 0 C

$$dS = \frac{\delta H}{T} = \frac{mL}{T}$$

$$= \frac{12.5 \times 10^{-3} \times 3.36 \times 10^5}{273}$$

$$= \mathbf{15.38 \; J/K}$$

(3) Increase in entropy when the temperature of 12.5 × 10 kg of water is raised from 0 C to 100 C (273 K to 373 K)

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \times 2.3026 \log_{10} \left(\frac{T}{T_1} \right)$$

$$= 12.5 \times 10^{-3} \times 4.2 \times 10^3 \times 2.3026 \log_{10} \left(\frac{373}{273} \right)$$

$= 16.38$ **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)

$$\Delta S = \frac{\delta H}{T} = \frac{mL}{T}$$

$$= \frac{12.5 \times 10^{-3} \times 2.25 \times 10^{6}}{373}$$

$= 75.4$ **J/K**

Total increase in entropy

$$= 2.42 + 15.38 + 16.38 + 75.4$$

$= 109.58$ **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 1997*]

[In C.G.S. 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/gm
$K = 0.005$ C.G.S. units
$\theta = 15$°C
$x_1 = 20$ cm
$x_2 = 30$ cm

$$t = \left[\frac{0.9 \times 80}{2 \times 0.005 \times 15} \right] \left[(30)^2 - (20)^2 \right]$$

$= 2.4 \times 10^{5}$ s

$=$ **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, $\frac{d\theta_1}{dt} = 2.6^\circ\text{C}$ per minute

Energy radiated per minute,

$$E_1 = m_1 s \left(\frac{d\theta_1}{dt}\right)$$

For first sphere,

$$m_1 \quad \left(\frac{4}{3}\pi R_1^3 S\right)$$

$$\frac{d\theta_1}{dt} = 2.6\ \text{C per minute}$$

Also $\quad E_1 \quad A_1 e \sigma t \left(T_1^4 - T_0^4\right)$

Here, $\quad T_1 = 273 + 121 = 394\ \text{K}$

$$T_0 \quad 273 + 30 = 303\ \text{K}$$

$$A_1 \quad 4\pi R_1^2$$

Similarly, for the second sphere

$$E_2 = m_2 s \left(\frac{d\theta_2}{dt}\right)$$

$$E_2 \quad A_2 e \sigma t \left(T_2^4 - T_0^4\right)$$

Here, $\quad A_2 \quad 4\pi R_2^2$

and $\quad m_2 \quad \frac{4}{3}\pi R$

$$T = 273 + 195 = 468\ \text{K}$$

$$\therefore \quad m_1 s \left(\frac{d\theta_1}{dt}\right) \quad A_1 e \sigma t \left(T_1^4 - T_0^4\right) \qquad \text{....(i)}$$

$$\text{and} \quad m_2 s \left(\frac{d\theta_2}{dt}\right) = A_2 e \sigma t \left(T_2^4 - T_0^4\right) \qquad \text{....(ii)}$$

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 $R_2 = 2R_1$

$$\frac{d\theta_2}{dt} = 2.6\left(\frac{1}{2}\right)(2.52)$$

$$= \textbf{3.276 °C per minute}$$

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, $\frac{d\theta}{dx} = 250$ °C m^{-1}

For $x = 0.05$ m

Temperature difference,

$$(\theta_1 - \theta_2) = 250 \times 0.05$$

$$= \textbf{12.5 °C}$$

(ii) $Q = KA\left(\frac{d\theta}{dx}\right)t$

For $t = 1$ second

$K = 384$ W m^{-1} K^{-1}

$A = 1$ m^2

$\frac{d\theta}{dx} = 250$ °C m^{-1} = 250 K m^{-1}

$Q = 384 \times 1\ (250)\ 1$

$$Q = 9.6 \times 10^4 \text{ J/s}.$$

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

$R_1 = \sigma T_1^4$

$R_2 = \sigma T_2^4$

$$\left(\frac{R_1}{R_2}\right) = \left(\frac{T_1}{T_2}\right)^4$$

$$= \left(\frac{200}{2000}\right)^4$$

$$= 10^{-4}$$

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* $= 6 \times 10^{-8}$ 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

$e = 1$

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

$$= 6 \times 10^{-8} \times 0.02 \times 1 \left[(500)^4 - (300)^4\right]$$

$$= \mathbf{65.28 \text{ J/s}}$$

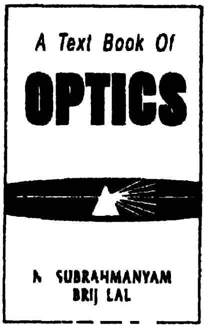
$$= \mathbf{65.28 \text{ watts}}$$

Index

BOOKS ON PHYSICS FOR DEGREE STUDENTS

N Subrahmanyam & Brij Lal

A TEXT-BOOK OF OPTICS



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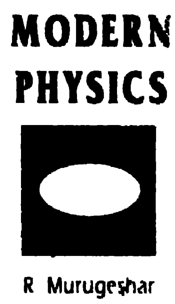

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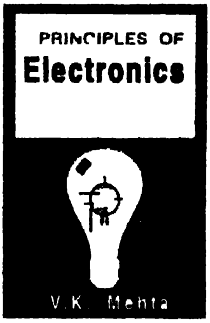

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