## 1·12 Constant Volume Hydrogen Thermometer

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).

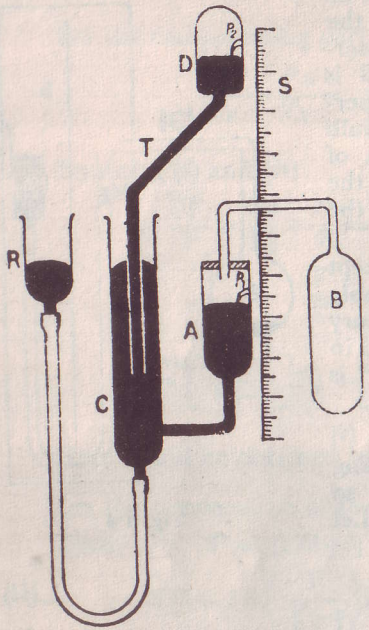


Fig. 1·5

**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 $\theta$°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 $\gamma$ 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,

$$\left\{\left(\frac{V_0(1+\gamma_0 t)+bh}{1+\gamma t}\right) + \frac{v}{1+\gamma\theta}\right\}\left(\frac{P_0+h}{76}\right) \qquad \ldots(ii)$$

Here, $\gamma_0$ 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 gas at NTP at 0 °C and $t$ °C. As the mass of the enclosed gas is constant, these two volumes must be equal.

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

$$V_0P_0 = \frac{\{V_0(1+\gamma_0 t)+bh\}(P_0+h)}{1+\gamma t} + \frac{vh}{1+\gamma\theta} \quad \ldots(iii)$$

or

$$\gamma t = \left(\frac{P_0+h}{P_0}\right)\left(\frac{V_0(1+\gamma_0 t)+bh}{V_0}\right) + \frac{hv}{P_0V_0}\left(\frac{1+\gamma t}{1+\gamma\theta}\right) - 1 \quad \ldots(iv)$$

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

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

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,

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

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

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

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

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



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

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

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

But from equation (*iii*),

$$P_tV_0 = (PV)_t$$

and

$$P_0V_0 = (PV)_0$$

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

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

Similarly it can be shown that

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

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

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

But in actual practice no gas is ideal.

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

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

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,

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

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 $P \to 0$ 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

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

$$\left.\begin{aligned} P_0V_0 &= A_0 + B_0P_0 \\ P_{100}V_0 &= A_{100} + B_{100}P_{100} \\ P_tV_0 &= A_t + B_tP_t \end{aligned}\right\} \qquad \ldots(ix)$$

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

$$t_v = \left(\frac{P_tV_0 - P_0V_0}{P_{100}V_0 - P_0V_0}\right) \times 100$$

$$\therefore \quad t_v = \left[\frac{(A_t + B_tP_t) - (A_0 + B_0P_0)}{(A_{100} + B_{100}P_{100}) - (A_0 + B_0P_0)}\right] \times 100$$

$$t_v = \left[\frac{(A_t - A_0) + (B_tP_t - B_0P_0)}{(A_{100} - A_0) + (B_{100}P_{100} - B_0P_0}\right] \times 100$$

$$t_v = \left(\frac{A_t - A_0}{A_{100} - A_0}\right) \times 100 \left[\frac{\left(1 + \frac{B_tP_t - B_0P_0}{A_t - A_0}\right)}{\left(1 + \frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0}\right)}\right]$$

$$t_v = \left(\frac{A_t - A_0}{A_{100} - A_0}\right) \times 100 \left(1 + \frac{B_tP_t - B_0P_0}{A_t - A_0}\right) \times \left(1 - \frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0}\right)$$

$$t_v = \left(\frac{A_t - A_0}{A_{100} - A_0}\right) \times 100 \left(1 + \frac{B_tP_t - B_0P_0}{A_t - A_0} - \frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0}\right) \qquad \ldots(x)$$

When $P \to 0$

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

$$\therefore \quad t_v = t_{lim}\left(1 + \frac{B_tP_t - B_0P_0}{A_t - A_0} - \frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0}\right) \qquad \ldots(xi)$$

$$\text{or} \quad t_{lim} - t_v = t_{lim}\left(\frac{B_{100}P_{100} - B_0P_0}{A_{100} - A_0} - \frac{B_tP_t - B_0P_0}{A_t - A_0}\right) \qquad \ldots(xii)$$



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 hot water.* (*Punjab 1966 ; Delhi 1973*)

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

$$P_{100} = 109{\cdot}3 \text{ cm of Hg}$$

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

$$t = \left(\frac{P_t - P_0}{P_{100} - P_0}\right) \times 100 = \left(\frac{100-80}{109{\cdot}3-80}\right) \times 100$$

$$t = \mathbf{68{\cdot}25°C}$$

**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

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

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

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

$$T = ?$$

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

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

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

$$T = \mathbf{819\ K = 546°C}$$



## 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 $\alpha$ and $\beta$ are constants. The values of $\alpha$ and $\beta$ depend on the nature of the material used. To find the values of $\alpha$ and $\beta$, 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

$$R_{444\cdot6} = R_0[1 + \alpha\,444{\cdot}6 + \beta(444{\cdot}6)^2] \qquad \ldots(iii)$$

The values of $\alpha$ and $\beta$ 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 $\beta t^2$ (because $\beta$ 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 $\rho$. 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 $O$.

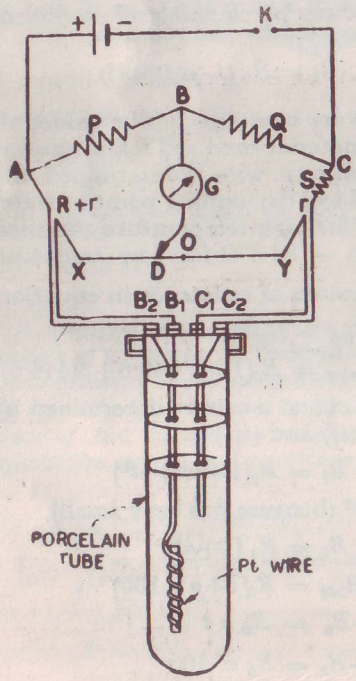


Fig. 1·6

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 $\beta t^2$ term has been neglected. Therefore, the correct thermodynamic temperature $\theta$ will differ from $t$.

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

The value of $\delta$ can be calculated by knowing the values of $\alpha$ and $\beta$.

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

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

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

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

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

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

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

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

The value of $\delta$ 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.

cause *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*)].

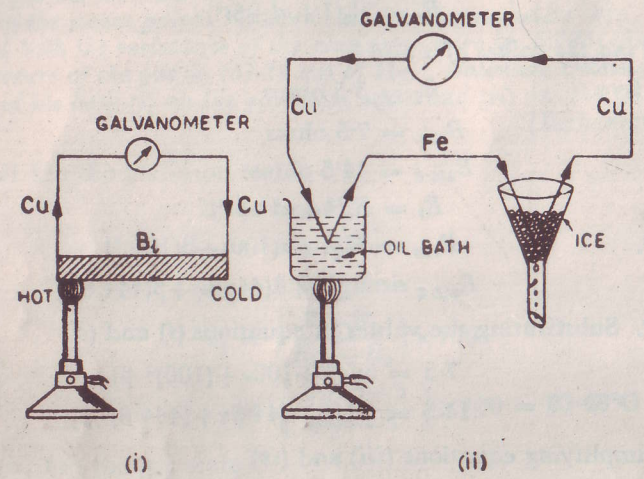


Fig. 1·7

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

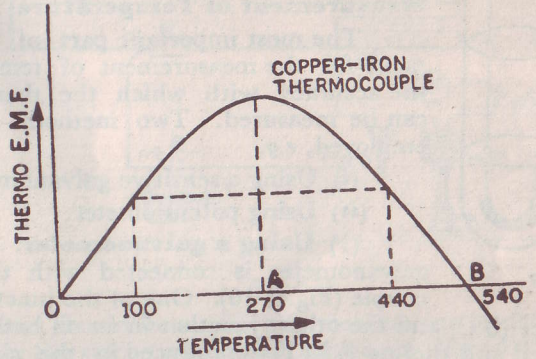


Fig. 1·8

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).

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.

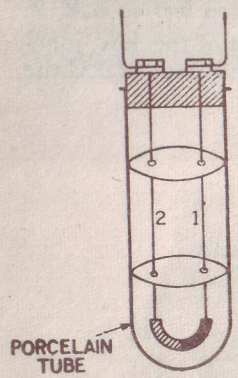


Fig. 1·9

**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 thermocouple (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.

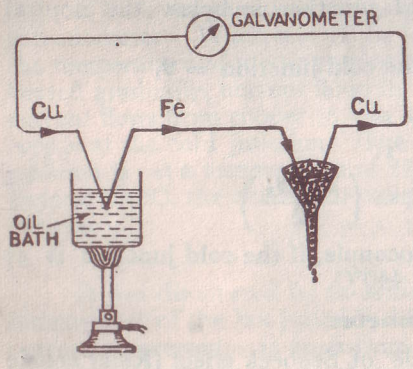


Fig. 1·10

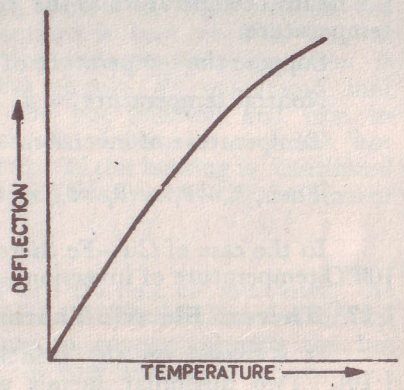


Fig. 1·11

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

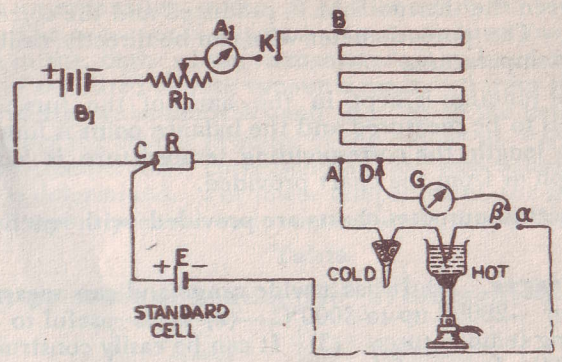


Fig. 1·12

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 $\alpha$. If on closing the key $K$, the deflection in the galvanometer decreases, then the connections are correct.

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 $\alpha$ 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.

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

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

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 $\alpha$ is taken out and the key $\beta$ 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 thermocouple.

**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).

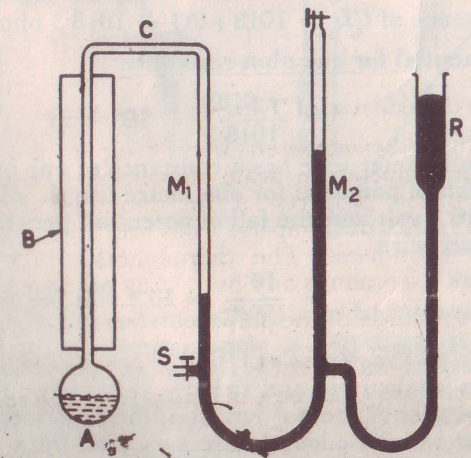


Fig. 1·13



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 | $1\ 6\times11^{-5}$ |
| 0·10 | $3{\cdot}4\times10^{-32}$ |

## 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

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

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 1974; 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 cm³. When the bulb is immersed in a bath, 200 cm³ 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]

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.

$$\therefore \text{ Useful heat } H = \frac{m(48{,}000)^2}{2 \times 2 \times 4{\cdot}2 \times 10^7} \text{ cals}$$

$$mS\theta = \frac{m(48{,}000)^2}{4 \times 4{\cdot}2 \times 10^7}$$

$$\theta = \frac{48{,}000 \times 48{,}000}{0{\cdot}03 \times 4 \times 4{\cdot}2 \times 10^7}$$

$$= \mathbf{457{\cdot}14°C}$$

**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 $6 \times 10^{23}$ atoms and sp. heat of aluminium = 0·22).*

Heat required to raise the temperature of 27 grams of aluminium by 1°C

$$= 27 \times 0{\cdot}22 \times 1 \text{ cal}$$

Energy gained by $6 \times 10^{23}$ atoms of aluminium

$$= 27 \times 0{\cdot}22 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$

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)*

$$h = 50 \text{ metres} = 5{,}000 \text{ cm}$$

Suppose, rise in temperature $= \theta$°C

Mass of water $= m$

Work done $= W = mgh$

$= m \times 980 \times 5{,}000$ ergs



Heat produced $= H = mS\theta$

$= m \times 1 \times \theta$ calories

$$W = JH$$

$$m \times 980 \times 5{,}000 = 4{\cdot}2 \times 10^7 \times m \times \theta$$

$$\theta = \frac{980 \times 5{,}000}{4{\cdot}2 \times 10^7}$$

$$= \mathbf{0{\cdot}117°C}$$

## 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 definite 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

$$PV = RT \qquad \text{...(i)}$$

and

$$\left[\frac{dU}{dP}\right]_T = 0 \qquad \text{...(ii)}$$

$$\left(\frac{dU}{dV}\right)_T = \left[\frac{dU}{dP}\right]_T \left[\frac{dP}{dV}\right]_T$$

From equation (i)

$$\frac{dP}{dV} = -\frac{RT}{V^2}$$

$$= -\left[\frac{RT}{V}\right]\left[\frac{1}{V}\right] = -\frac{P}{V}$$

$$\therefore \quad \left(\frac{dU}{dV}\right)_T = \left[\frac{dU}{dP}\right]_T \left[-\frac{P}{V}\right]_T \qquad \text{...(iii)}$$

As $\left(-\frac{P}{V}\right)$ is not equal to zero and

$$\left[\frac{dU}{dP}\right]_T = 0$$

$$\therefore \quad \left[\frac{dU}{dV}\right]_T = 0 \qquad \text{...(iv)}$$

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.

$$\therefore \quad U = f(T) \qquad \text{...(v)}$$

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*.

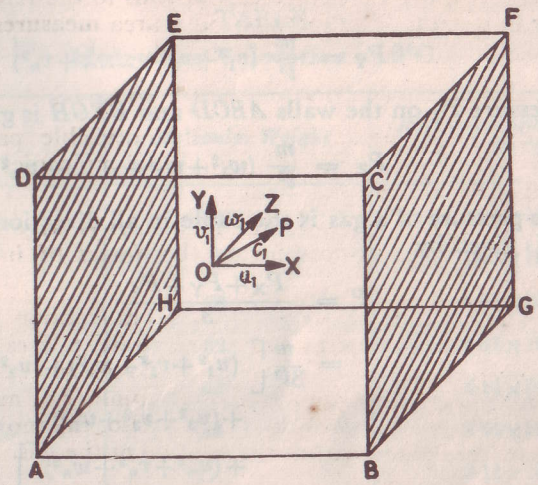


Fig. 5·7

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

$$P = \frac{P_X+P_Y+P_Z}{3}$$

$$= \frac{m}{3l^3}\Big[(u_1^2+v_1^2+w_1^2)+(u_2^2+v_2^2+w_2^2)+(u_3^2+v_3^2+w_3^2)+\ldots\ldots+(u_n^2+v_n^2+w_n^2)\Big]$$

$$= \frac{m}{3l^3}\Big[C_1^2+C_2^2+C_3^2+\ldots\ldots C_n^2\Big] \quad \ldots(i)$$

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

$$P = \frac{m.nC^2}{3V} \quad \ldots(ii)$$

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 $V$.

$$\therefore \quad P = \frac{MC^2}{3V}$$

or $$P = \frac{1}{3}\rho C^2 \quad \ldots(iii)$$

$$\because \quad \frac{M}{V} = \rho \text{ the density of the gas.}$$

From equation (*iii*)

$$C^2 = \frac{3P}{\rho}$$



or $$C = \sqrt{\frac{3P}{\rho}} \quad \ldots(iv)$$

**[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 | $18{\cdot}4\times10^4$ |
| Helium | 4 | $13{\cdot}1\times10^4$ |
| Nitrogen | 28 | $4{\cdot}95\times10^4$ |
| Oxygen | 32 | $4{\cdot}61\times10^4$ |
| Argon | 40 | $4{\cdot}14\times10^4$ |
| Carbon dioxide | 44 | $3{\cdot}95\times10^4$ |
| Chlorine | 71 | $3{\cdot}11\times10^4$ |

**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 :

$$C = \sqrt{\frac{3P}{\rho}}$$

$$= \sqrt{\frac{3\times76\times13{\cdot}6\times981}{0{\cdot}000089}}$$

$$= 1{\cdot}84\times10^5 \text{ cm/s}$$

(*b*) For oxygen the density at N.T.P.

$$= 16\times0{\cdot}000089$$

$$\therefore \quad C \text{ for oxygen} = \sqrt{\frac{3\times76\times13{\cdot}6\times981}{16\times0{\cdot}000089}}$$

$$= 4{\cdot}6\times10^4 \text{ cm/s}$$

(*c*) For air the density at N.T.P. is 0·001293 g/cc

$$\therefore \quad C \text{ for air} = \sqrt{\frac{3\times76\times13{\cdot}6\times981}{0{\cdot}001293}}$$

$$= \mathbf{4{\cdot}850\times10^4 \text{ cm/s}}$$

**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/cm³
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 $= n$

$$\therefore \quad P = \frac{1}{3} mnC^2$$

$$n = \frac{3P}{mC^2}$$

Here
$$P = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$m = 52{\cdot}8 \times 10^{-24} \text{ g}$$
$$C = 4{\cdot}62 \times 10^4 \text{ cm/s}$$

$$\therefore \quad n = \frac{3 \times 76 \times 13{\cdot}6 \times 980}{52{\cdot}8 \times 10^{-24} \times (4{\cdot}62 \times 10^4)^2}$$

$$\mathbf{n = 2{\cdot}697 \times 10^{19}}$$

## 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. $\rho$ 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

$$PV = RT$$
$$\therefore \quad \frac{1}{3} MC^2 = RT$$
$$\frac{1}{2} MC^2 = \frac{3}{2} RT \qquad \ldots(i)$$



Let the mass of each molecule be $m$ and Avogadro's number be $N$.

$$M = m \times N$$
$$\frac{1}{2} mNC^2 = \frac{3}{2} RT$$
$$\frac{1}{2} mC^2 = \frac{3}{2}\frac{R}{N} T$$
$$= \frac{3}{2} k T \qquad \ldots(ii)$$

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 $P = 76 \times 13{\cdot}6 \times 980$ dynes/cm²

$\rho = 16 \times 0\ 000089$

$$\therefore \quad C = \sqrt{\frac{3 \times 76 \times 13{\cdot}6 \times 980}{16 \times 0{\cdot}000089}}$$

$$C = 4{\cdot}6 \times 10^4 \text{ cm/s}$$

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 $C = 4{\cdot}6 \times 10^4$ cm/s

$T = 273$ K

$T_1 = 27°C$

$= 27 + 273$

$= 300$ 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 $N \times k = R$

$$\therefore \quad PV = RT \qquad \text{...(ii)}$$

*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 $P = 76 \times 13{\cdot}6 \times 980$ 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 $= v$

$$= \frac{24610 \times 3{\cdot}2}{32}$$

$$= 2461 \text{ cc}$$

## 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 $\quad PV = \text{const.}$ —at constant temperature.

(*ii*) *Charles' Law*

According to the kinetic theory

$$P = \frac{1}{3}\rho C^2$$

$$P = \frac{1}{3}\frac{M}{V}C^2$$

$$PV = \frac{1}{3}MC^2$$

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*),

$$\therefore \quad PV = NkT \qquad \ldots(ii)$$

where $N$ is the Avogadro's number and $k$ is the Boltzmann's constant.

If $\quad P$ 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 $\quad R = Nk$

$$PV = NkT.$$

Let $n$ be the number of molecules per cc. In that case,

$$P = nkT$$

$$\therefore \quad n = \frac{P}{kT}$$

But $\quad k = \frac{R}{N}$

$$\therefore \quad n = \frac{PN}{RT}$$

**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 $\quad P = 76 \times 13{\cdot}6 \times 980$ dynes/cm$^2$

$N = 6{\cdot}023 \times 10^{23}$

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

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

$$x = \frac{76 \times 13{\cdot}6 \times 980 \times 6{\cdot}023 \times 10^{23} \times 10^{6}}{8{\cdot}31 \times 10^{7} \times 273}$$

$$\mathbf{x = 2{\cdot}688 \times 10^{25}}$$

**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

$$P = 3 \times 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$N = 6{\cdot}023 \times 10^{23}$$
$$R = 8{\cdot}31 \times 10^{7} \text{ ergs/g mol-K}$$
$$T = (273 + 136{\cdot}5)$$
$$= 409{\cdot}5 \text{ K}$$

$$\therefore \quad x = \frac{3 \times 76 \times 13{\cdot}6 \times 980 \times 6{\cdot}023 \times 10^{23} \times 10^{3}}{8{\cdot}31 \times 10^{7} \times 409{\cdot}5}$$

$$\mathbf{x = 5{\cdot}376 \times 10^{22}}$$

**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

$$n_1 = 2{\cdot}7 \times 10^{19}$$
$$P_1 = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$
$$P_2 = 10^{-6} \text{ mm of Hg}$$
$$= 10^{-7} \text{ cm of Hg}$$
$$P_2 = 10^{-7} \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$n_2 = \frac{2{\cdot}7 \times 10^{19} \times 10^{-7} \times 13{\cdot}6 \times 980}{76 \times 13{\cdot}6 \times 980}$$

$$\mathbf{n_2 = 3{\cdot}553 \times 10^{10}}$$

(*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

$$n_2 = 3{\cdot}553 \times 10^{10}$$
$$T_2 = 0° \text{ C}$$
$$= 273 \text{ K}$$
$$T_3 = 39° \text{ C}$$
$$= 273 + 39$$
$$= 312 \text{ K}$$

$$\therefore \quad n_3 = \frac{3{\cdot}553 \times 10^{10} \times 273}{312}$$

$$\mathbf{n_3 = 3{\cdot}109 \times 10^{10}}$$

## 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 $= n_1$

$$\frac{C_2}{C_1} = \sqrt{\frac{T_2}{T_1}}$$

Here $C_2 = \frac{C_1}{2}$

$T_2 = ?$

$T_1 = 273$ K

$$\therefore \quad \frac{1}{2} = \sqrt{\frac{T_2}{273}}$$

$$\frac{1}{4} = \frac{T_2}{273}$$

$$T_2 = \frac{273}{4} = 68{\cdot}25 \text{ K}$$

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 mono-atomic 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

$$\frac{1}{2} mC^2 = \frac{3}{2} kT \qquad \text{...(i)}$$

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 $\frac{1}{2} m(u^2) = \frac{1}{2} m(v^2) = \frac{1}{2} m(w^2)$

$$\therefore \quad \frac{1}{2} mC^2 = 3\left[\frac{1}{2} m(u^2)\right] = 3\left[\frac{1}{2} m(v^2)\right]$$

$$= 3\left[\frac{1}{2} m(w^2)\right]$$

$$= \frac{3}{2} kT$$

$$\therefore \quad \frac{1}{2} mu^2 = \frac{1}{2} kT \qquad \text{...(ii)}$$

$$\frac{1}{2} mv^2 = \frac{1}{2} kT \qquad \text{...(iii)}$$

$$\frac{1}{2} mw^2 = \frac{1}{2} kT \qquad \text{...(iv)}$$

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 $C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{3}{2} R + R = \frac{5}{2} R$$

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 $\gamma$ 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 $\gamma$, $C_P$ 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 $du$.

$$\therefore \quad \frac{dN_x}{N} = f(u)du$$

$$\therefore \quad dN_x = N\,f(u)\,du$$

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

$$\frac{d^2N_{x,y}}{dN_x} = \frac{dN_y}{N} = f(v)dv$$

$$\therefore \quad d^2N_{x,y} = N\,f(u)\,f(v)du\,dv$$

The number of molecules represented by $d^2N_{x,y}$ is still large. Suppose that the fraction of these molecules $d^2N_{x,y,z}$ 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 $\rho$ is constant *i.e.*, velocity space is isotropic.

Also $\quad C^2 = u^2+v^2+w^2$

$$\therefore \quad Nf(u)\,f(v)\,f(w) = \text{const.} \qquad \ldots(i)$$

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 $\beta$ is an arbitrary, unknown function. The product $m\beta$ is called Langrange undetermined multiplier.

$$\therefore \quad m\beta[udu+vdv+wdw] = 0 \qquad \ldots(vii)$$

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 $(xi)$, $\beta$ would either be a constant or a function of the variable in that equation. A constant value of $\beta$ 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

$$\rho = NA^3 e^{-\beta[\frac{1}{2}m(u^2+v^2+w^2)]}$$

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 $\rho$ is constant within the infinitesimal spherical shell within the radii $c$ and $c+dc$. The volume of this element is $4\pi c^2 dc$. This volume element contains $dN$ molecules.

$$\therefore \qquad \rho = \frac{dN}{4\pi c^2\, dc} \qquad \ldots(xviii)$$

From equations (*xvi*) and (*xviii*)

$$\frac{dN}{4\pi c^2 dc} = NA^3\, e^{-\beta[\frac{1}{2}mc^2]}$$

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*)

$$\frac{dN}{dc} = 4\pi N\left[\frac{m}{2\pi kT}\right]^{3/2} c^2\, e^{-\frac{mc^2}{2kT}}$$

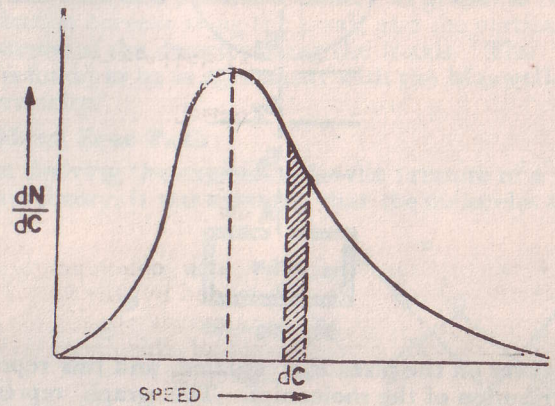


Fig. 5·8

$$\frac{dN}{dc} = \frac{4N}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} c^2\, e^{-\frac{mc^2}{2kT}} \qquad \ldots(xxi)$$

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 $S_3$. 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

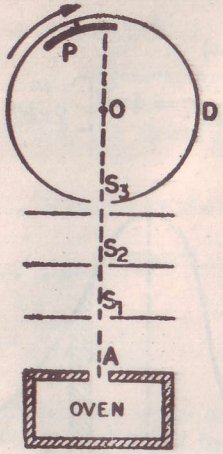


Fig. 5·9

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.

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

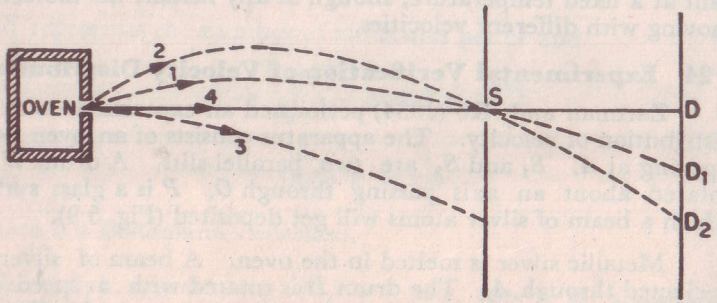


Fig. 5·10

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.



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

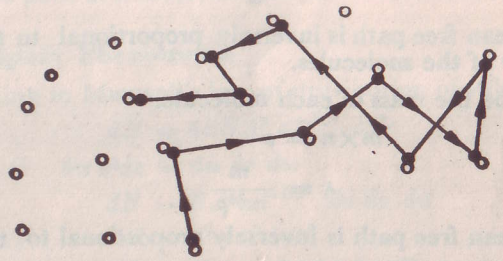

Fig. 5·11

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 $\lambda$ is given by

$$\lambda = \frac{S}{N} \qquad \ldots(i)$$

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, $\quad m \times n = \rho$

$$\lambda = \frac{m}{\pi d^2 \rho} \qquad \ldots(iii)$$

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 $\lambda$ on the basis of the law of distribution of velocities

TABLE

**Mean Free Path ($\lambda$)**

| *Gas* | $d$ | $\lambda$ |
|---|---|---|
| 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

$$dN = 4\pi N A^3 e^{-bc^2} c^2 dc \qquad \ldots(i)$$

But $\quad 4\pi c^2 dc = du\, dv\, dw$

$$dN = N A^3 e^{-bc^2} du\, dv\, dw \qquad \ldots(ii)$$

Also $\quad c^2 = u^2 + v^2 + w^2$

$$\therefore \qquad dN = N A^3 e^{-b(u^2+v^2+w^2)} du\, dv\, dw \qquad \ldots(iii)$$

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 $\quad W = w - w_0$

From equation (iii), Maxwell's law of distribution of velocity can be written as

$$dN = N A^3 e^{-b(U^2+V^2+W^2)} dU\, dV\, dW \ldots(iv)$$

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 $\lambda$ of a molecule. *A molecule moving through a free path $\lambda$ is actually transferring momentum, energy and mass through a distance $\lambda$.*

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.

$$F = -\eta A \frac{du}{dx} \qquad \text{...(i)}$$

Here $\eta$ 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



$\lambda$, then the distance for the first collision to occur $= (x-\lambda)$. The average velocity of these molecules $= (x-\lambda)\frac{du}{dx}$.

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 $= \frac{1}{6} nC$.

Mass of the molecules $= \frac{1}{6} mnC = M$

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

$$F = M(x-\lambda)\frac{du}{dx} - M(x+\lambda)\frac{du}{dx}$$

$$F = -2M\lambda\frac{du}{dx}$$

$$F = -2\left[\frac{1}{6} mnC\right]\lambda\frac{du}{dx}$$

$$= -\frac{1}{3} mnC\lambda\frac{du}{dx} \qquad \text{...(ii)}$$

Comparing (i) and (ii)

$$\eta A\frac{du}{dx} = \frac{1}{3} mnC\lambda\frac{du}{dx}$$

But $A = 1$ sq cm

$$\therefore \quad \eta = \frac{1}{3} mnC\lambda \qquad \text{...(iii)}$$

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

$$\eta = \frac{1}{3} mnC\frac{1}{\sqrt{2}\,\pi\sigma^2 n}$$

$$\eta = \frac{mC}{3\sqrt{2}\,\pi\sigma^2} \qquad \text{...(iv)}$$

But $\qquad C \propto \sqrt{T}$

$\therefore \qquad \eta \propto \sqrt{T} \qquad \ldots(v)$

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 $\lambda$. 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).

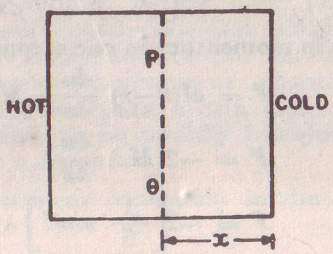


Fig. 5·12

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

$$= MC_v\left(\theta + \frac{d\theta}{dx}\lambda\right)$$



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

$$H = MC_v\left[\theta + \frac{d\theta}{dx}\lambda\right] - MC_v\left[\theta - \frac{d\theta}{dx}\lambda\right]$$

$$H = 2MC_v\lambda\frac{d\theta}{dx} \qquad \ldots(i)$$

$$\therefore \qquad H = 2\left[\frac{1}{6}mnC\right]C_v\lambda\frac{d\theta}{dx}$$

$$H = \frac{1}{3}mnC.C_v\lambda\frac{d\theta}{dx} \qquad \ldots(ii)$$

From the definition of thermal conductivity

$$H = KA.\frac{d\theta}{dx}.t$$

Here $\qquad A = 1$ sq cm

$\qquad t = 1$ second

$$\therefore \qquad H = K.\frac{d\theta}{dx} \qquad \ldots(iii)$$

Comparing (*ii*) and (*iii*)

$$K = \frac{1}{3}mnC.C_v.\lambda \qquad \ldots(iv)$$

$$K = \frac{1}{3}mnC.C_v \times \frac{1}{\sqrt{2}.\pi\sigma^2 n}$$

$$= \frac{mC.C_v}{3\sqrt{2}.\pi\sigma^2} \qquad \ldots(v)$$

But $\qquad C \propto \sqrt{T}$

$\therefore \qquad K \propto \sqrt{T}$

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

Below the Boyle temperature, the gases are highly compressible and this suggests the existence of inter-molecular attractions. Beyond

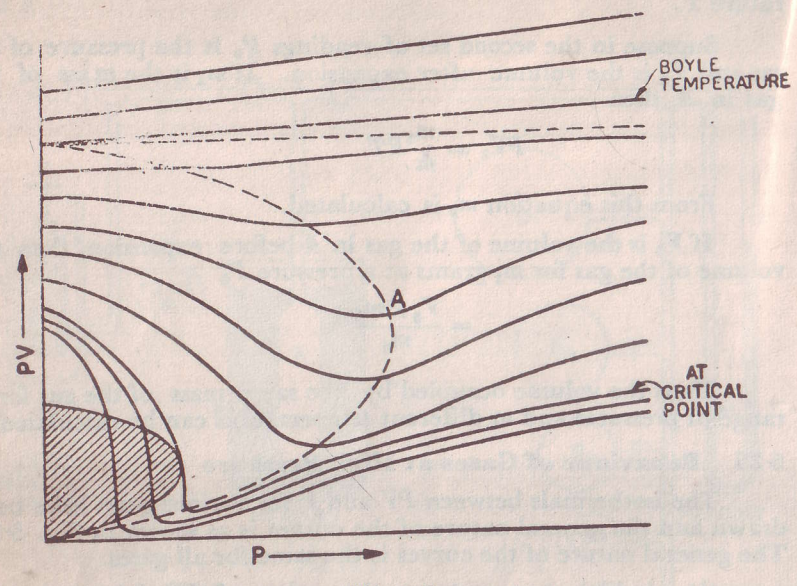


Fig. 5·18.

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.

$$\therefore \text{ Correction for pressure } p \propto \rho^2 \propto \frac{1}{V^2}$$

$$p = \frac{a}{V^2}$$



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 $n$th 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

$$= V - \frac{nS}{2} \qquad (\text{But } S = 8x)$$

$$= V - \frac{n(8x)}{2}$$

$$= V - 4(nx)$$

$$= V - b$$

$\therefore$ $b = 4(nx)$ = 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

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad \text{...(ii)}$$

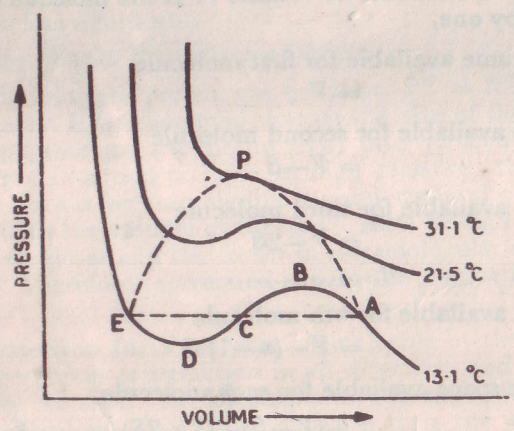


Fig. 5·19

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

$$\left(P + \frac{a}{V^2 T}\right)(V - b) = RT$$

## 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 $\frac{d^2P}{dV^2} = 0$,

$$T = T_c,$$

$$V = V_c$$

$$\therefore \quad \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0$$

$$\frac{6a}{V_c^4} = \frac{2RT_c}{(V_c-b)^3} \qquad \ldots(v)$$

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

$$\frac{V_c}{3} = \frac{V_c-b}{2}$$

or

$$2V_c = 3V_c-3b$$

$$V_c = 3b \qquad \ldots(vi)$$

Substituting the value of

$$V_c = 3b \text{ in equation } (iv)$$

$$\frac{2a}{27b^3} = \frac{RT_c}{4b^2}$$

or

$$T_c = \frac{8a}{27\,Rb} \qquad \ldots(vii)$$

Substituting these values of $V_c$ and $T_c$ in equation (*ii*)

$$P_c = \frac{R \times 8a}{27\,Rb(2b)} - \frac{a}{9b^2}$$

$$P_c = \frac{a}{27b^2} \qquad \ldots(viii)$$

## 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 | 2·26 |
| Hydrogen | —240°C | 12·80 |
| Nitrogen | —146°C | 33·50 |
| Air | —140°C | 39·00 |
| Argon | —122°C | 48·00 |
| Oxygen | —118°C | 50·00 |
| Carbon dioxide | 31°C | 73·00 |
| Ammonia | 130°C | 15·00 |
| Chlorine | 146°C | 76·00 |
| Water | 374°C | 218·00 |

## 5·39 Coefficient of Van der Waals Constants

$$V_c = 3b \qquad \ldots(i)$$

$$P_c = \frac{a}{27b^2} \qquad \ldots(ii)$$

$$T_c = \frac{8a}{27\,Rb} \qquad \ldots(iii)$$

From equations (*iii*) and (*ii*)

$$\frac{T_c^2}{P_c} = \frac{64\,a^2}{(27)^2\,R^2b^2} \times \frac{27b^2}{a}$$

$$= \frac{64a}{27\,R^2}$$

$$\therefore \quad a = \frac{27}{64}\,\frac{R^2T_c^2}{P_c} \qquad \ldots(iv)$$

Dividing (*iii*) by (*ii*)

$$\frac{T_c}{P_c} = \frac{8a}{27\,Rb} \times \frac{27b^2}{a}$$

$$= \frac{8b}{R}$$

$$b = \frac{RT_c}{8P_c} \qquad \ldots(v)$$

Also

$$\frac{RT_c}{P_cV_c} = \frac{R\,(8a)\,.\,27b^2}{27\,Rb\,a\,(3b)}$$

$$\frac{RT_c}{P_cV_c} = \frac{8}{3} \qquad \ldots(vi)$$

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 | 51 | 2·25 | 15·4 | 3·13 |
| Hydrogen | 33·1 | 12·8 | 32·2 | 3·28 |
| Nitrogen | 125·9 | 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*

95 $T_c = 132$ K, $P_c = 37{\cdot}2$ *atmospheres*,

*R per mole* $= 82{\cdot}07$ 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 $$a = 13{\cdot}31 \times 10^6 \text{ atmos cm}^6$$



(ii) $$b = \frac{RT_c}{8P_c}$$

$$b = \frac{82{\cdot}07 \times 132}{8 \times 37{\cdot}2}$$

or $$b = 36{\cdot}41 \text{ cm}^3$$

## 5·40 Reduced Equation of State

Taking the pressure, volume and temperature of a gas in terms of reduced pressure, volume and temperature,

$$\frac{P}{P_c} = \alpha,\ \frac{V}{V_c} = \beta,\ \frac{T}{T_c} = \gamma$$

$$P = \alpha\,P_c,\ V = \beta\,V_c,\ T = \gamma\,T_c$$

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 $\alpha$, $\beta$ and $\gamma$ 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.

# 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 $\theta_1$ and $\theta_2$ where $\theta_1 > \theta_2$. Heat is conducted in the direction of the fall of temperature. Quantity of heat conducted across the two opposite faces

$$Q \propto A$$

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

$$Q \propto t$$

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

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

or

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

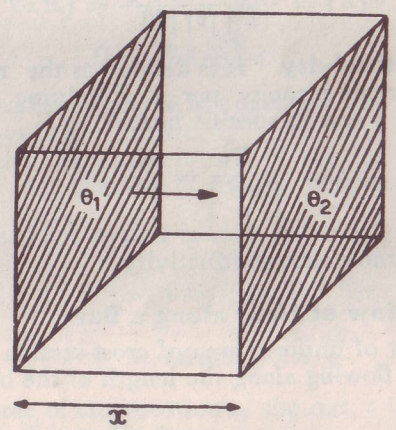


Fig. 8·1

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

If $A = 1$ sq cm, $(\theta_1 - \theta_2) = 1°C$, $t = 1$ s, $x = 1$ cm

then $$Q = K$$

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

**Temperature gradient.** The quantity $\frac{\theta_1 - \theta_2}{x}$ represents the rate of fall of temperature with respect to distance. The quantity $\frac{d\theta}{dx}$

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

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

**Dimensions** of K

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

$Q$ represents energy and its dimensions are,

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

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

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

**Thermal Diffusivity.** It is defined as the ratio of thermal conductivity to thermal capacity per unit volume. Let the density of the substance be $\rho$ and its specific heat $S$.

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

$h$ is also called thermometric conductivity.

### 8·3 Rectilinear Flow of Heat along a Bar

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

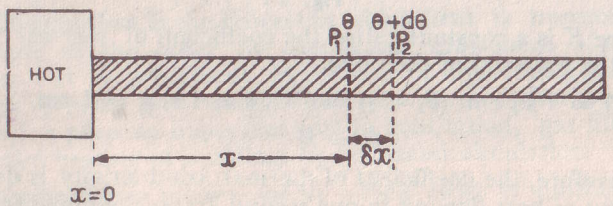


Fig. 9·2

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



surroundings) of the bar at $P_1$. The excess of temperature at $P_2 = \theta + \frac{d\theta}{dx}\delta x$

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

Heat flowing through $P_1$ in one second

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

Heat flowing through $P_2$ in one second

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

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

$$Q = Q_1 - Q_2$$

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

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

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

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

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

where $A$ is the area of cross-section of the rod, $\rho$ is the density of the material and $S$ is the specific heat.

The heat lost per second due to radiation

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

where $E$ is the emissive power of the surface, $p$ is the perimeter and $\theta$ 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

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

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

**Special Cases**

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

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

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

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

The general solution of this equation is

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

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 $\theta_0$ and of the other end be zero.

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

From equation (*ix*)

$$\theta_0 = A + B$$

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

From equation (*ix*),

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



But $e^{\infty}$ cannot be zero, therefore

$$A = 0$$

Taking $A = 0$

$$\theta_0 = B$$

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

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

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

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

At $x = 0$

$$\theta = \theta_0$$

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

The values of $A$ and $B$ in this case are

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

and

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

The solution of equation (*ix*) will be

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

## 8·4 Ingen-Hausz Experiment

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

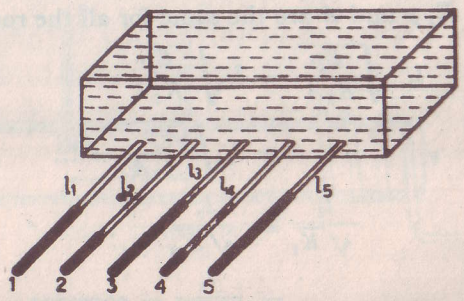


Fig. 8·3

Take a box containing hot water or oil. Rods of different materials of the same length and area of cross-section (same size and

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 $\theta_1$, $\theta_2$, $\theta_3$ and $\theta_4$.

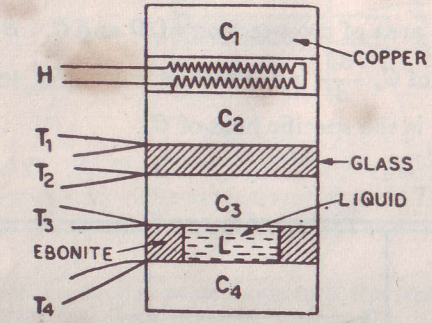


Fig. 8·14

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

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

Heat flowing per second through the liquid and the ebonite ring

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

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

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

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



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

Consider two thin spherical shells $A$ and $B$ of radii $r_1$ and $r_2$. The specimen is contained between these two shells $A$ and $B$ (Fig. 8·15). A heating element is placed at the centre of the shells. Heat is conducted through the specimen from the inner to the outer shell. Let the temperatures of the inner and the outer shells be $\theta_1$ and $\theta_2$, after the steady state is reached.

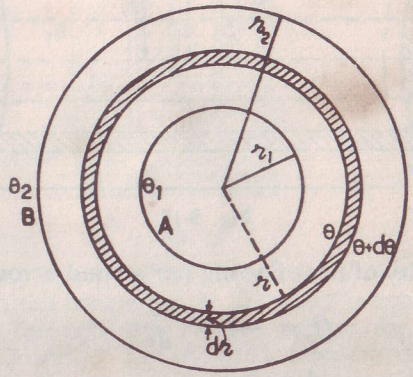


Fig. 8·15

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

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

Here $\quad A = 4\pi r^2$

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

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

Integrating,

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

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

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

$K$ is calculated from equation (*ii*).

## 8·12 Cylindrical Flow of Heat

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

the inner surface is $\theta_1$ and on the outer surface it is $\theta_2$. 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).

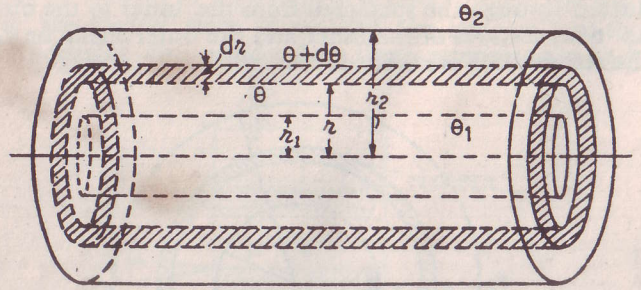


Fig. 8·16

The quantity of heat flowing per second across the element

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

But $$A = 2\pi rl$$

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

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

$Q$ is constant after the steady state is reached.

Integrating equation (*i*)

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

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

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

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

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

## 8·13 Thermal Conductivity of Rubber

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



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

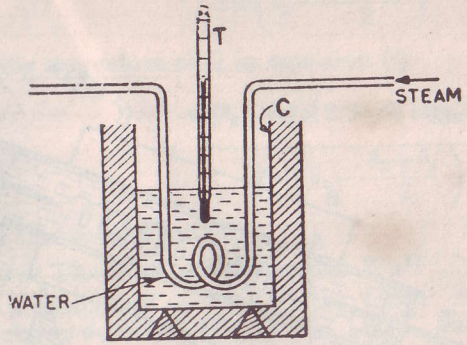


Fig. 8·17

a known length (say 50 cm) of it is immersed in water as shown in Fig. 8·17. The initial temperature of water is noted. Let it be $\theta_3$. Steam is passed through the rubber tubing for a known time $t$ seconds (say 900 seconds). Let the final temperature of water be $\theta_4$ (after applying radiation correction) and temperature of steam be $\theta_1$. 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 $\theta_2$ and $Q$

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

Thus, $K$ for rubber can be calculated.

## 8·14 Thermal Conductivity of Glass

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

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

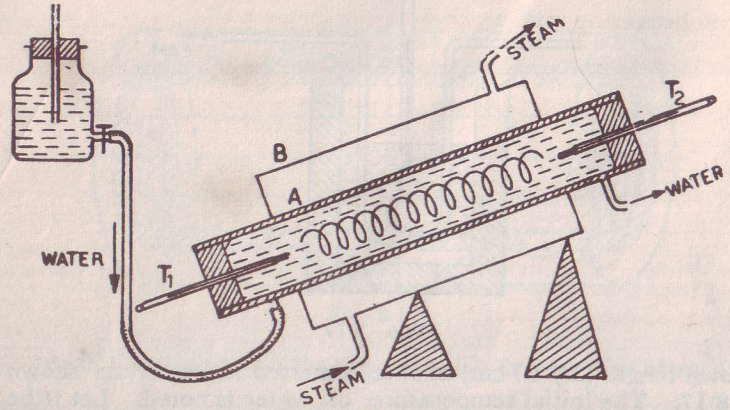


Fig. 8·18

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

Suppose,

Length of the tube inside the jacket $= l$

Temperature of steam $= \theta_1$

Temperature of incoming water $= \theta_3$

Temperature of outgoing water $= \theta_4$

Mass of water collected $= m$

Time taken $= t$ seconds

Quantity of heat gained by water in $t$ seconds

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

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

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

Average temperature of the inside of the glass tube

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



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

Substituting the values of $Q$ in equation (i)

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

Hence, $K$ can be determined.

## 8·15 Heat Flow Through a Compound Wall

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

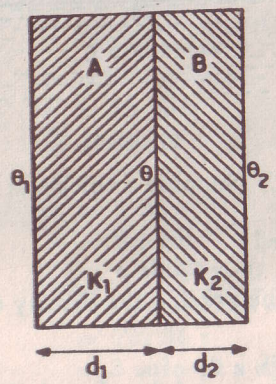


Fig. 8·19

For the material $A$,

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

For the meterial $B$,

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

From equations (i) and (ii),

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

$$\theta = \frac{\frac{K_1\theta_1}{d_1} + \frac{K_2\theta_2}{d_2}}{\frac{K_1}{d_1} + \frac{K_2}{d_2}} = \frac{d_2K_1\theta_1 + d_1K_2\theta_2}{d_2K_1 + d_1K_2}$$

Substituting the value of $\theta$ in equation (*i*),

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

In general, for any number of walls or slabs,

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

## 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 over the surface of ice be $-\theta$°C and that

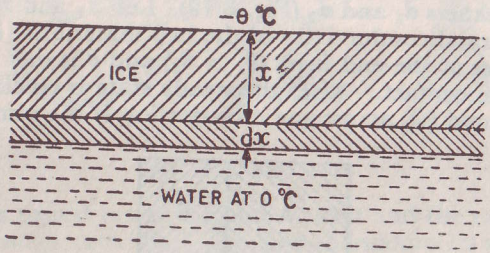


Fig. 8·20

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

Mass of ice formed

$$= A.dx.\rho$$

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

Heat lost by water

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

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

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

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

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

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

$\frac{dx}{dt}$ 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 $x$

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

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

When $t = 0,\ x = 0$

Hence the constant is zero.

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

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

*Thermal conductivity of ice = 0·005*

*Latent heat of ice = 80* cal/g

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

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

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

Here $\rho = 0{\cdot}91$ g/cm³

$L = 80$ cal/g

$K = 0{\cdot}005$

$\theta = 20$°C

$x_1 = 3$ cm

$x_2 = 3{\cdot}1$ cm

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

$= 222{\cdot}04$ s

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

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

$K = 0{\cdot}005$

$L = 80$ cal/g

$\rho = 0{\cdot}90$ g/cm³

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

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

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

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

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

## 8·17 Wiedemann-Franz Law

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

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

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

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

or

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

This law holds good for a large number of metals between +100°C and −100°C. At low temperatures the ratio $K/\sigma$ 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 | 2·43 |



## 8·18 Practical Applications of Conduction of Heat

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

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

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

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

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

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

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

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

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

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

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

## 8·19 Davy's Safety Lamp

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

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 $$F_1[P_A, V_A, P_B, V_B] = 0 \qquad ...(i)$$

Expression $(i)$ can be solved, and

$$P_B = f_1[P_A, V_A, V_B] \qquad ...(ii)$$

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 $$P_B = f_2[V_B, P_C, V_C] \qquad ...(iii)$$

From equations $(ii)$ and $(iii)$ for $A$ and $C$ to be in thermal equilibrium separately,

$$f_1(P_A, V_A, V_B) = f_2[V_B, P_C, V_C] \qquad ...(iv)$$

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.

$$\therefore\ F_3[P_A, V_A, P_C, V_C] = 0. \qquad ...(v)$$

Equation $(iv)$ contains a variable $V_B$, whereas equation $(v)$ does not contain the variable $V_B$. It means

$$\phi_1(P_A, V_A) = \varphi_3(P_C, V_C) \qquad ...(vi)$$



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.

$$\therefore \quad H+H' = 0$$

$$H = -H' \qquad \ldots(iv)$$

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 $\delta H$.

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.

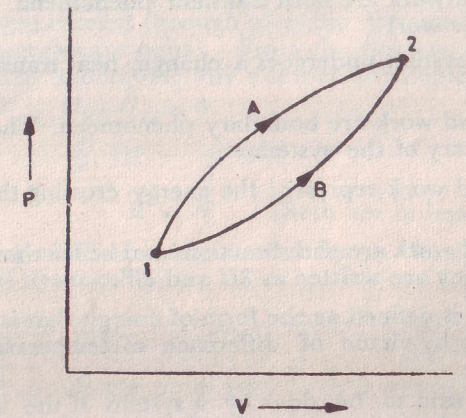


Fig. 6·1

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 $\delta W$ 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 $\delta H$ and $\delta W$.

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 $\delta H$, the amount of external work done be $\delta W$ 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

$$\delta H = dU + \delta W \qquad ...(i)$$

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 $$\oint \delta H = \oint \delta w \qquad ...(ii)$$

[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

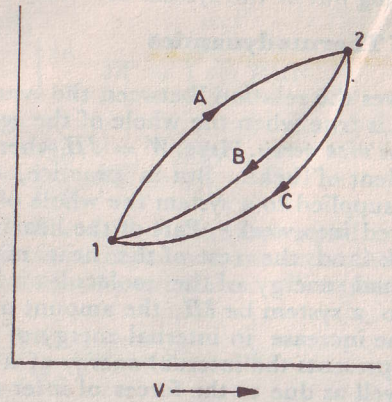


Fig. 6·2

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).

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.

$$\therefore \qquad \delta H - \delta W = dE \qquad \ldots(iv)$$

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. ${}_1H_2$ 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 (v)

$$\delta H = dU + \delta W \qquad ...(vi)$$

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.*

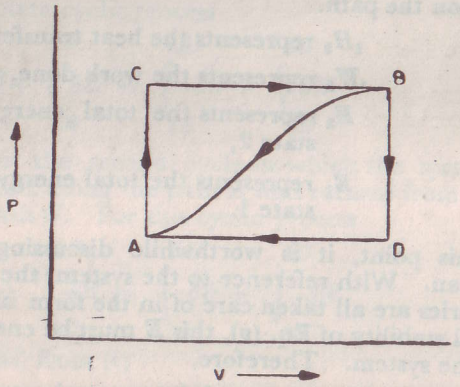


Fig. 6·3

Along the path $ACB$,

$$H_{ACB} = U_B - U_A + W$$

Here $\quad H = +80$ joules

$\quad W = +30$ joules

$\therefore \quad +80 = U_B - U_A + 30$

$$U_B - U_A = 80 - 30 = \mathbf{50\ joules}$$

(a) Along the path $ADB$,

$$W = +10 \text{ joules}$$



$$H_{ADB} = U_B - U_A + W$$

$$H = 50 + 10 = \mathbf{60\ joules}$$

(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) $\quad U_A = 0, \qquad U_D = 40$ joules

$$U_B - U_A = 50$$

$\therefore \quad U_B = 50$ 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,

$$U = f(V, T) \qquad ...(i)$$

Differentiating equation (i)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \qquad ...(ii)$$

If an amount of heat $\delta H$ 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 $\quad \delta W = P.dV$

$\therefore \quad \delta H = dU + P.dV$

Substituting the value of $dU$ from equation (ii)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \qquad ...(iii)$$

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 $$\left(\frac{\delta H}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dV}{dT} \quad ...(iv)$$

If the gas is heated at constant volume,

$$\left(\frac{\delta H}{\partial T}\right)_V = C_V$$

and $$\frac{dV}{dT} = 0$$

$$\therefore \left(\frac{\delta H}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \quad ...(v)$$

When the gas is heated at constant pressure,

$$\left(\frac{\delta H}{dT}\right)_P = C_P$$

$\therefore$ 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 $$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \quad ...(vi)$$

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 $$P\left(\frac{\partial V}{\partial T}\right)_P = R \quad ...(vii)$$

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\therefore \quad C_P - C_V = R \quad ...(viii)$$



Here $C_P$, $C_V$ and $R$ are expressed in the same units.

From equation $(iii)$

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \quad ...(ix)$$

For a process at constant temperature

$$dT = 0$$

$$\therefore \quad (\delta H)_T = P(dV)_T + \left(\frac{\partial U}{\partial V}\right)_T (dV)_T \quad ...(x)$$

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 $dV$,

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \quad ...(xii)$$

The isobaric volume coefficient of expansion

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \alpha V = \left(\frac{\partial V}{\partial T}\right)_P$$

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad \frac{C_P - C_V}{\alpha V} = P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0 = P - P$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{C_P - C_V}{\alpha V}\right) - P \quad ...(xiii)$$

or $$-\left(\frac{C_P - C_V}{\alpha V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \quad ...(xiv)$$

From equations (*xii*) and (*xiv*)

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left(\frac{C_P - C_V}{\alpha V}\right)$$

or

$$\left(\frac{\partial T}{\partial V}\right) = \frac{C_V - C_P}{\alpha V C_V} \qquad \ldots(xv)$$

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

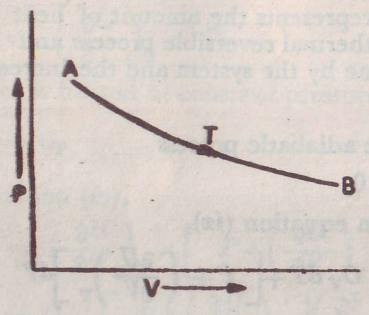


Fig. 6·4

an isothermal process. Consider a working substance at a certain pressure and temperature and having a volume represented by the point *A* (Fig. 6·4).

Pressure is decreased and work is done by the working substance at the cost of its internal energy and there should be fall in temperature. But, 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 heat from the surroundings. When work is done on the working



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

$$\delta H = C_v dT$$

$$\therefore \quad C_v dT = dU \qquad \ldots(ii)$$

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 $\delta H$ 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,

$$\delta H = 1 \times C_v dT + \frac{P \cdot dV}{J} \quad \text{...(i)}$$

But
$$\delta H = C_p . dT \quad \text{...(ii)}$$
$$P.dV = r.dT$$

$$\therefore \quad C_p dT = C_v . dT + \frac{r.dT}{J}$$

$$C_p - C_v = \frac{r}{J} \quad \text{...(iii)}$$

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

$$C_p - C_v = \frac{R}{J} \quad \text{...(iv)}$$

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 $\delta W$.

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.

$$\therefore \quad 0 = dU + \frac{P.dV}{J} \quad \text{...(i)}$$

As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by $dT$.

$$dU = 1 \times C_v \times dT$$

$$C_v . dT + \frac{P.dV}{J} = 0 \quad \text{...(ii)}$$

For an ideal gas

$$PV = rT \quad \text{...(iii)}$$

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,
$$\frac{r}{J} = C_p - C_v$$



$$\therefore \quad C_v . P.dV + C_v . V.dP + C_p . PdV - C_v PdV = 0$$

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

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
$$PV^\gamma = \text{const.} \quad \text{...(iv)}$$

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.

$$rTV^{\gamma-1} = \text{const.}$$

$$\therefore \quad TV^{\gamma-1} = \text{const.} \quad \text{...(v)}$$

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
$$\frac{P^{\gamma-1}}{T^\gamma} = \text{const.} \quad \text{...(vi)}$$

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, $P_1 = 2$ atmospheres

$$T_1 = 273+27 = 300 \text{ K}$$

$$P_2 = 1 \text{ atmosphere}$$

$$T_2 = ?$$

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

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

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

$$\left(\frac{1}{2}\right)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

$$0{\cdot}4 \log (0.5) = 1{\cdot}4 [\log T_2 - \log 300]$$

$$-0{\cdot}1204 = 1{\cdot}4 \log T_2 - 3{\cdot}4680$$

$$1{\cdot}4 \log T_2 = 3{\cdot}4680 - 0{\cdot}1204 = 3{\cdot}3476$$

$$\log T_2 = \frac{3{\cdot}3476}{1{\cdot}4} = 2{\cdot}3911$$

$$T_2 = 246{\cdot}1 \text{ K} = -26{\cdot}9°\text{C}$$

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**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

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$P_2 = P_1\left[\frac{V_1}{V_2}\right]^{\gamma} = 1[2]^{1.4} = 2{\cdot}636 \text{ atmospheres}$$

(ii) $V_1 = V$ ; $V_2 = \frac{V}{2}$.

$$T_1 = 300 \text{ K} ; T_2 = ?$$

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

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

$$T_2 = T_1[2]^{1.4-1} = 300[2]^{0.4} = 395{\cdot}9 \text{ K} = 122{\cdot}9°\text{C}$$



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**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 $\gamma$ for air $= 1{\cdot}40$

$$T_2 = T_1[2]^{1.40-1}$$

$$T_2 = T_1[2]^{0.40}$$

$$T_2 = 1{\cdot}319\, T_1$$

Change in temperature

$$= T_2 - T_1 = 1{\cdot}319\, T_1 - T_1 = \mathbf{0{\cdot}319\, T_1\ K}$$

**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, $P_2 = 50$,

$$P_1 = 1,$$

$$T_1 = 273+27 = 300 \text{ K}$$

$$T_2 = ?$$

$$\gamma = \frac{5}{3}$$

$$\therefore \quad (50)^{2/3} = \left(\frac{T_2}{300}\right)^{5/3}$$

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 $\gamma$ 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 $V_1 = V, \quad V_2 = \frac{V}{3}$

$T_1 = 300$ 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 $$T_2 = 300 \left[\frac{3V}{V}\right]^{\gamma-1}$$

$$= 300\,[3]^{1.4-1}$$

or $$T_2 = 465{\cdot}5 \text{ K}$$

$$= 192{\cdot}5 \text{ °C}$$

The temperature of air increases by

192·5—27 = **165·5 °C** or **165·5 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. $\gamma$ for the gas is 1·40.*

[*Delhi (Hons.) 75*]

(1) Here, $V_1 = V, \quad V_2 = 3V$

$T_1 = 273$ K $\quad T_2 = ?$

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

or $$T_2 = T_1 \left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$T_2 = 273 \left[\frac{1}{3}\right]^{1.4-1}$$

$$T_2 = \mathbf{176\ K = -97°C}$$

(2) Here, $V_1 = V, \quad V_2 = 3V$

$P_1 = 1$ atmosphere, $\quad P_2 = ?$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$P_2 = P_1 \left[\frac{V_1}{V_2}\right]^{\gamma}$$

or $$P_2 = 1 \left(\frac{1}{3}\right)^{1.4}$$

$$P_2 = \mathbf{0{\cdot}2148\ atmosphere}$$



## 6·16 Slopes of Adiabatics and Isothermals

In an isothermal process

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

Differentiating,

$$PdV + VdP = 0$$

or $$\frac{dP}{dV} = -\frac{P}{V} \qquad \text{...(i)}$$

In an adiabatic process

$$PV^{\gamma} = \text{const.}$$

Differentiating,

$$P\gamma V^{\gamma-1}\, dV + VdP = 0$$

$$\frac{dP}{dV} = -\frac{\gamma P}{V} \qquad \text{...(ii)}$$

Therefore, the slope of an adiabatic is $\gamma$ times the slope of the isothermal.

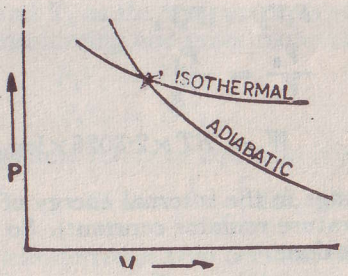


Fig. 6·5

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 $V_2$,

Work done $$= \int_{V_1}^{V_2} P \,.\, dV = \text{area } ABba \qquad \text{...(i)}$$

Fig. 6·6 represents the indicator diagram. Considering one gram molecule of the gas

$$PV = RT$$

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

$$\therefore \quad W = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

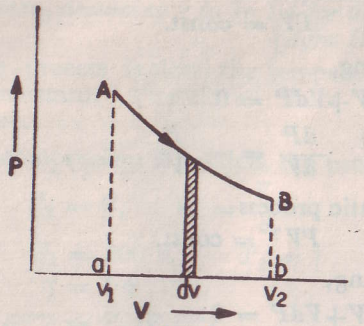


Fig. 6·6

$$= RT \log_e \frac{V_2}{V_1} \qquad \ldots(ii)$$

$$W = RT \times 2{\cdot}3026 \log_{10} \frac{V_2}{V_1} \qquad \ldots(iii)$$

Also $\quad P_1V_1 = P_2V_2$

or $\quad \dfrac{V_2}{V_1} = \dfrac{P_1}{P_2}$

$$\therefore \quad W = RT \times 2{\cdot}3026 \times \log_{10} \frac{P_1}{P_2} \qquad \ldots(iv)$$

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

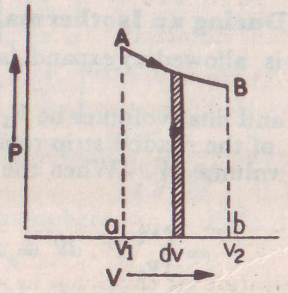


Fig. 6·7.

for an increase in 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 $\quad P = \dfrac{K}{V^{\gamma}}$

$$W = K \int_{V_1}^{V_2} \frac{dV}{V^{\gamma}}$$

$$= \frac{1}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right] \qquad \ldots(i)$$

Since $A$ and $B$ lie on the same adiabatic

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

$$W = \frac{1}{1-\gamma}\left[\frac{K}{V_2^{\gamma-1}} - \frac{K}{V_1^{\gamma-1}}\right]$$

$$W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] \qquad \ldots(ii)$$

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 $\quad P_2V_2 = RT_2$

Substituting these values in equation (ii)

$$W = \frac{1}{1-\gamma}\left[RT_2 - RT_1\right] \qquad \ldots(iii)$$

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 $\quad \dfrac{V.dP}{-dV} = P \qquad \ldots(i)$

From the definition of elasticity of a gas

$$E_{iso} = \frac{dP}{-dV/V}$$

$$= \frac{VdP}{-dV} \qquad \ldots(ii)$$

From (*i*) and (*ii*)

$$E_{iso} = P \qquad \ldots(iii)$$

**2. Adiabatic Elasticity**

During an adiabatic process

$$PV^{\gamma} = \text{const}$$

Differentiating, $P\gamma V^{\gamma-1}dV + V^{\gamma}dP = 0$

or

$$\frac{VdP}{-dV} = \gamma P \qquad \ldots(iv)$$

From the definition of elasticity of a gas

$$E_{adi} = \frac{dP}{-dV/V}$$

$$= \frac{V.dP}{-dV} \qquad \ldots(v)$$

From (*iv*) and (*v*),

$$E_{adi} = \gamma P \qquad \ldots(vi)$$

Comparing (*iii*) and (*vi*)

$$E_{adi} = \gamma E_{iso}$$

Thus, the adiabatic elasticity of a gas is $\gamma$ times the isothermal elasticity.

## 6·20 Clement and Desormes Method—Determination of $\gamma$

Clement and Desormes in 1819 designed an experiment to find $\gamma$, the ratio between the two specific heats of a gas.

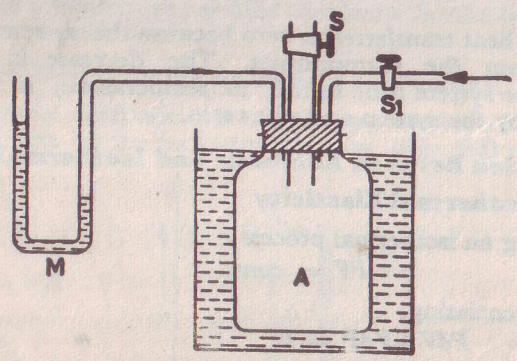


Fig. 6·8

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.

$$P_1V_1 = P_2V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \qquad \ldots(ii)$$

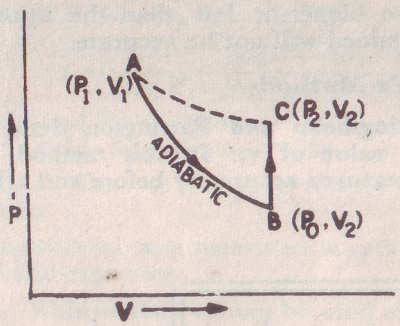


Fig. 6·9

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,

$$\log P_1 - \log P_0 = \gamma[\log P_1 - \log P_2]$$

$$\gamma = \frac{\log P_1 - \log P_0}{\log P_1 - \log P_2} \qquad \ldots(iii)$$

## 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 flywheel rotating with an angular velocity $\omega$. 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 rises 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 principl e 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 $\omega$. 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

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.

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**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.

### 6·26 Carnot's Reversible Engine

1824

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.*

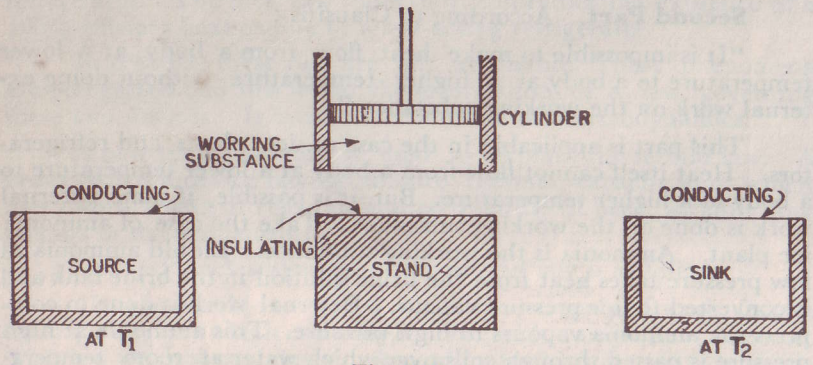


Fig. 6·12

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

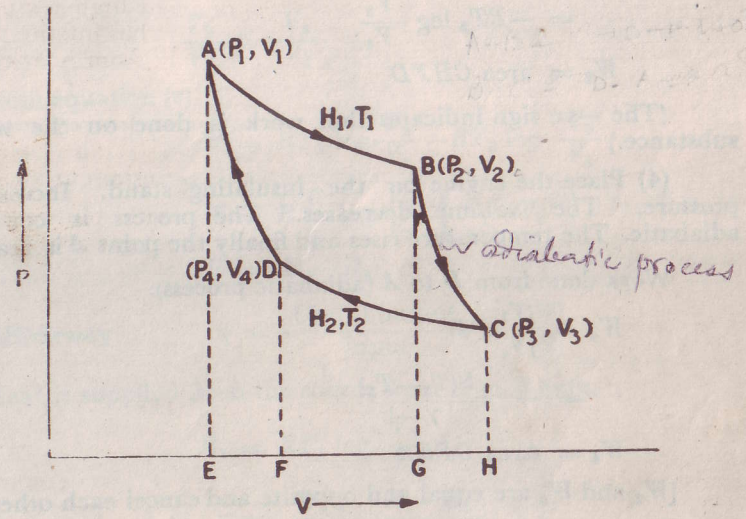


Fig. 6·13

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).

Work done from $B$ to $C$ (adiabatic process)

$$W_2 = \int_{V_2}^{V_3} P\,.\,dV$$

$$= K\int_{V_2}^{V_3} \frac{dV}{V^\gamma}$$

$$= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma}$$

$$= \frac{P_3V_3 - P_2V_2}{1-\gamma}$$

$$= \frac{R[T_2 - T_1]}{1-\gamma} = \frac{R[T_1 - T_2]}{\gamma - 1}$$

$$W_2 = \text{Area } BOHG \qquad \ldots(ii)$$

But $PV^\gamma = \text{constant} = K$

$P_2V_2 = RT_1$

$P_3V_3 = RT_2$

$P_3V_3^\gamma = P_2V_2^\gamma = K$

(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)

$$W_3 = \int_{V_3}^{V_4} PdV$$

$$= RT_2 \log \frac{V_4}{V_3}$$

$$= -RT_2 \log \frac{V_3}{V_4} \qquad \ldots(iii)$$

$$W_3 = \text{area } CHFD$$

(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).

$$W_4 = \int_{V_4}^{V_1} PdV$$

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

$$W_4 = \text{Area } DFEA \qquad \ldots(iv)$$

[$W_2$ 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

$$= H_1 - H_2$$

$$\text{Net work} = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \log \frac{V_2}{V_1} + \frac{R(T_1-T_2)}{\gamma-1} - RT_2 \log \frac{V_3}{V_4} - \frac{R[T_1-T_2]}{\gamma-1}$$

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \qquad \ldots(v)$$

The points $A$ and $D$ are on the same adiabatic

$$T_1V_1^{\gamma-1} = T_2V_4^{\gamma-1}$$

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



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 $(v)$

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

$$W = R\left[\log \frac{V_2}{V_1}\right]\left[T_1 - T_2\right]$$

$$\therefore \quad W = H_1 - H_2$$

**Efficiency** $$\eta = \frac{\text{Useful output}}{\text{Input}} = \frac{W}{H_1}$$

Heat is supplied from the source from $A$ to $B$ only.

$$H_1 = RT_1 \log \frac{V_2}{V_1}$$

$$\therefore \quad \eta = \frac{W}{H_1} = \frac{H_1 - H_2}{H_1}$$

$$= \frac{R[T_1-T_2] \log\left(\frac{V_2}{V_1}\right)}{RT_1 \log\left(\frac{V_2}{V_1}\right)}$$

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.

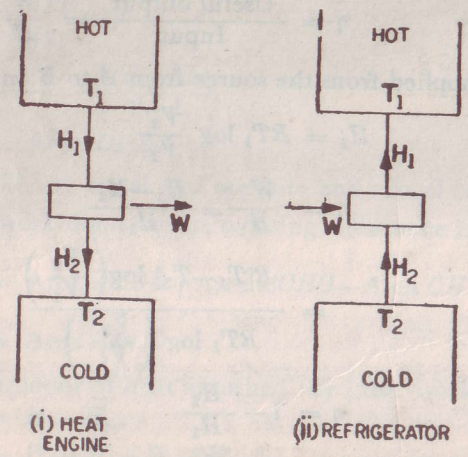


Fig. 6·14

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.*

$$H_1 = 200 \text{ cal}; \qquad H_2 = 150 \text{ cal}$$

$$T_1 = 400 \text{ K}; \qquad T_2 = ?$$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$T_2 = \frac{H_2}{H_1} \times T_1$$

$$T_2 = \frac{150}{200} \times 400 = \mathbf{300 \text{ K}}$$

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

$$= 1 - \frac{300}{400} = 0{\cdot}25$$

% efficiency = **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).*

$T_1 = 450$ K ; $T_2 = 350$ K

$H_1 = 1000$ cal ; $H_2 = ?$

$$\frac{H_2}{H_1} = \frac{T_2}{T_1}$$

$$H_2 = H_1 \times \frac{T_2}{T_1}$$

$$= \frac{1000 \times 350}{450} = \mathbf{777{\cdot}77\ cals}$$

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

$$= 1 - \frac{350}{450} = \frac{100}{450}$$

$$= 0{\cdot}2222$$

% efficiency = **22·22%**

Work done in each cycle

$$= H_1 - H_2$$

$$= 1000 - 777{\cdot}77$$

$$= 222{\cdot}23 \text{ cal}$$

$$= 222{\cdot}23 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{933{\cdot}33\ joules}$$

**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*]

$H_1 = ?$ $H_2 = 500$ cal

$T_1 = 300$ K $T_2 = 260$ K

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} ;$$



$$H_1 = H_2 \cdot \frac{T_1}{T_2}$$

$$H_1 = \frac{500 \times 300}{260} = 576{\cdot}92 \text{ cal}$$

$$W = H_1 - H_2 = 76{\cdot}92 \text{ cal}$$

$$= 76{\cdot}92 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{323{\cdot}08\ joules}$$

**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*]

$H_1 = ?$

$H_2 = 1000 \times 80 = 80{,}000$ cal

$T_1 = 300$ K

$T_2 = 273$ K

(1) $$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$H_1 = \frac{H_2 T_1}{T_2}$$

$$= \frac{80{,}000 \times 300}{273}$$

$$H_1 = \mathbf{87{,}900\ Cal}$$

(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 $$W = \mathbf{3{\cdot}183 \times 10^4\ joules}$$

(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

$$\eta = 50\% = 0{\cdot}5, \quad T_2 = 273+7 = 280 \text{ K}.$$

$$T_1 = ?$$

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

or $$0{\cdot}5 = 1 - \frac{280}{T_1}$$

or $$T_1 = 560\ K$$

In the second case

$$\eta' = 70\% = 0{\cdot}7,$$

$$T_2 = 280\ K,$$

$$T_1' = ?$$

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

$$0{\cdot}7 = 1 - \frac{280}{T_1'}$$

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 $A$

$$= \eta = \frac{H_1 - H_2}{H_1} = \frac{W}{H_1}$$

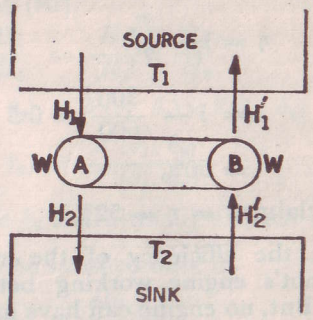


Fig. 6·15.

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, $\eta$ cannot be greater than $\eta'$. 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 $\theta_1$ and $\theta_2$. Here $H_1$ is the heat absorbed at $\theta_1$ and $H_2$ is the heat rejected at $\theta_2$

$$\eta = f(\theta_1, \theta_2)$$

$$\eta = \frac{H_1 - H_2}{H_1} = f(\theta_1, \theta_2)$$

$$\therefore \quad 1 - \frac{H_2}{H_1} = f(\theta_1, \theta_2)$$

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 $\theta_2$ and $\theta_3$ 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 $\theta_1$ and $\theta_3$ 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 $\theta_3$ 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 $\phi$ 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 $\theta_1/\theta_2$.

$$\therefore \quad \frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \qquad \ldots(iv)$$

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 $CD$ 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

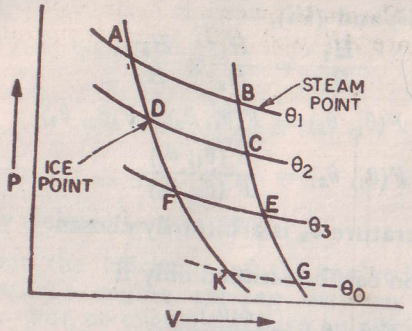


Fig. 6·16

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 $\quad \eta = \dfrac{H_1 - H_2}{H_1} = 1 - \dfrac{H_2}{H_1}$

If $\quad 1 - \dfrac{H_2}{H_1} = 1, \dfrac{H_2}{H_1} = 0$ 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

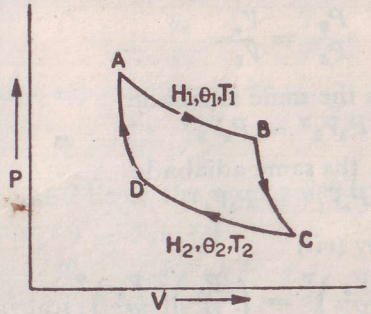


Fig. 6·17

scale is $\theta_1$ and the ideal scale is $T_1$ for the isothermal $AB$ and the temperature on the work scale is $\theta_2$ 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.

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 $(ii)$

$$\frac{H_1}{H_2} = \frac{rT_1 \log \dfrac{V_2}{V_1}}{rT_2 \log \dfrac{V_3}{V_4}} \quad \ldots(iii)$$

Also, $A$ and $B$ lie on the same isothermal

$$P_1V_1 = P_2V_2$$

or
$$\frac{P_2}{P_1} = \frac{V_1}{V_2} \qquad ...(iv)$$

$C$ and $D$ lie on the same isothermal

$$P_3V_3 = P_4V_4$$

or
$$\frac{P_3}{P_4} = \frac{V_4}{V_3} \qquad ...(v)$$

$B$ and $C$ lie on the same adiabatic

$$P_2V_2^{\gamma} = P_3V_3^{\gamma} \qquad ...(vi)$$

$A$ and $D$ lie on the same adiabatic

$$P_1V_1^{\gamma} = P_4V_4^{\gamma} \qquad ...(vii)$$

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
$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \qquad ...(viii)$$

Substituting this value in equation $(iii)$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2} \qquad ...(ix)$$

From the work scale of temperature,

$$\frac{H_1}{H_2} = \frac{\theta_1}{\theta_2} \qquad ...(x)$$

$$\therefore \quad \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2} \qquad ...(xi)$$

**Special considerations.** $(i)$ If $\theta_1$ 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 $\quad \theta_{steam} = T_{steam}$

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 $\rho$

$$\rho = \frac{V_3}{V_2}$$

The points $B$ and $C$ lie on the same adiabatic

$$\therefore \quad T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$$

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

$$= \left(\frac{1}{\rho}\right)^{\gamma-1}$$

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

## 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

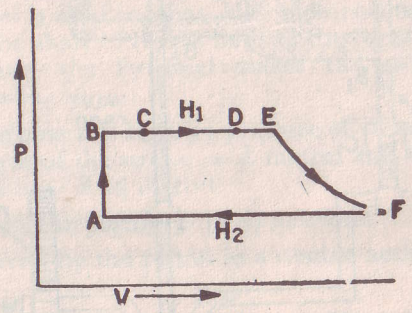


Fig. 6·18

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.

Here $H_1 = +1000$ 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 $H_2 = 600$ joules

$$\sum \frac{H}{T} = \frac{H_1}{T_1} + \frac{H_2}{T_2}$$

Here $H_1 = +1000$ 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

$$\oint \frac{\delta H}{T} = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \ldots(i)$$



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 $(ii)$

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2C}^{1C} \frac{\delta H}{T} \qquad \ldots(iii)$$

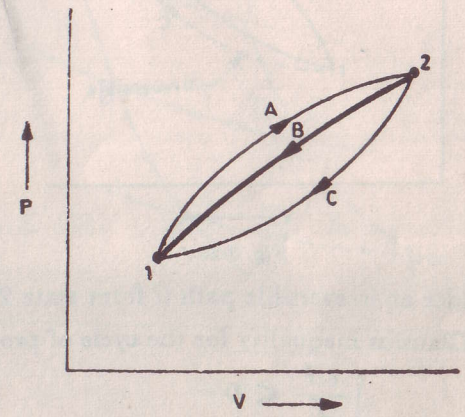


Fig. 6·25

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

$$\oint \delta H = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \ldots(i)$$

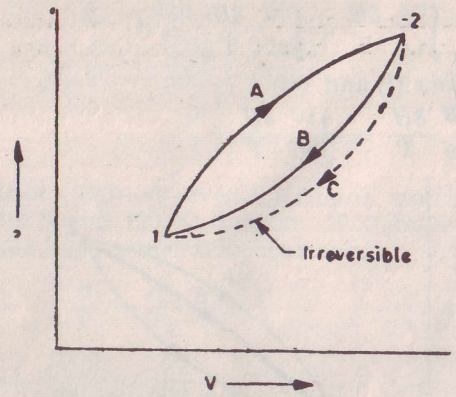


Fig. 6·26

Now consider an irreversible path $C$ from state 2 to state 1.

Applying Clausius inequality for the cycle of processes $A$ and $C$

$$\int \frac{\delta H}{T} < 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} < 0 \qquad \ldots(ii)$$

From equations $(i)$ and $(ii)$

$$\int_{2B}^{1B} \frac{\delta H}{T} - \int_{2C}^{1C} \frac{\delta H}{T} > 0$$

Since path $B$ is reversible and entropy is a property

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2B}^{1B} dS = \int_{2C}^{1C} dS$$

$$\therefore \quad dS > \frac{\delta H}{T} \qquad \ldots(iii)$$

or

$$S_2 - S_1 > \int_1^2 \delta H \qquad \ldots(iv)$$

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

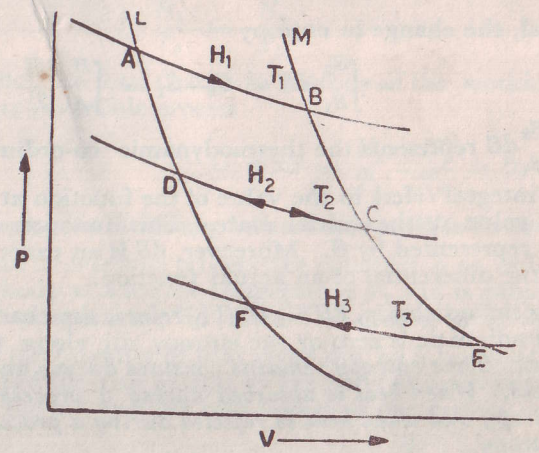


Fig. 6·27

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 $T_2$.

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Similarly considering the cycle $DCEF$

$$\frac{H_2}{T_2} = \frac{H_3}{T_3}$$

$$\therefore \quad \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_3}{T_3} = \text{constant}$$

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 $\delta H$ at a temperature $T$,

Change in entropy

$$dS = \frac{\delta H}{T} \qquad ...(1)$$

In general, the change in entropy

$$= \int_{S_1}^{S_2} dS = S_2 - S_1 = \int_A^B \frac{\delta H}{T} \qquad ...(2)$$

$\int_A^B \frac{\delta H}{T} = \int_{S_1}^{S_2} dS$ 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

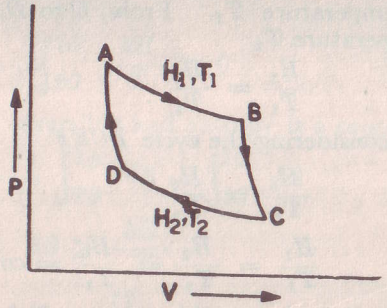


Fig. 6·28



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 o,f 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

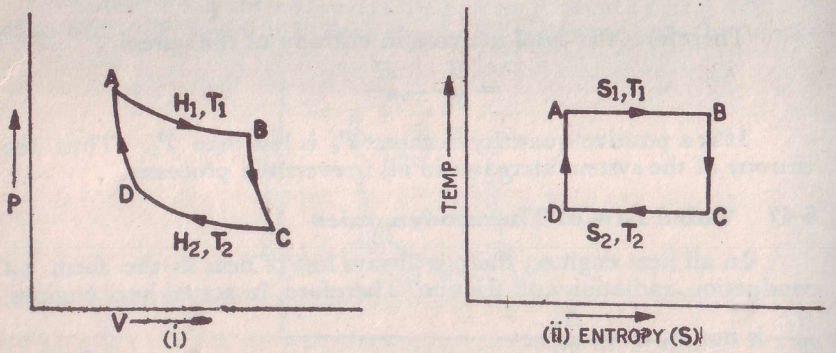


Fig. 6·29

*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.

The area *ABCD* in the temperature-entropy diagram represents the actual amount of energy converted into work [Fig. 6·29 (*ii*)].

The area $ABCD = S_1(T_1-T_2) = S_2(T_1-T_2)$

But $S_1 = \dfrac{H_1}{T_1}$ and $S_2 = \dfrac{H_2}{T_2}$



Here $S_1 = S_2 = \dfrac{H_1}{T_1} = \dfrac{H_2}{T_2} = \dfrac{H_1-H_2}{T_1-T_2}$

$\therefore$ Area $ABCD = \dfrac{(H_1-H_2)(T_1-T_2)}{T_1-T_2} = H_1-H_2$

Therefore, the area *ABCD* represents the energy converted to work

Efficiency $= \dfrac{H_1-H_2}{H_1} = 1-\dfrac{H_2}{H_1} = 1-\dfrac{T_2}{T_1}$

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 $\delta H$.

$$\delta H = dU+\delta W$$

$$\delta H = 1\times C_V\times dT+\frac{PdV}{J} \qquad ...(i)$$

$$\delta H = TdS$$

$$\therefore \quad TdS = C_V dT+\frac{PdV}{J} \qquad ...(ii)$$

Also $PV = rT$

or $P = \dfrac{rT}{V}$

$$\therefore \quad TdS = C_V dT+\frac{rT.dV}{JV}$$

$$dS = C_V\frac{dT}{T}+\frac{r}{J}\frac{dV}{V}$$

Integrating, $\displaystyle\int_{S_1}^{S_2} dS = C_V\int_{T_1}^{T_2}\frac{dT}{T}+\frac{r}{J}\int_{V_1}^{V_2}\frac{dV}{V}$

$$S_2-S_1 = C_V\log_e\frac{T_2}{T_1}+\frac{r}{J}\log_e\frac{V_2}{V_1} \qquad ...(iii)$$

$$S_2-S_1 = C_v\times 2{\cdot}3026\log_{10}\frac{T_2}{T_1}+\frac{r}{J}\times 2{\cdot}3026\log_{10}\frac{V_2}{V_1} \qquad ...(iv)$$

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 $\quad C_V + \frac{r}{J} = C_P$

$$\therefore \quad dS = C_P \frac{dT}{T} - \frac{VdP}{JT}$$

Also $\quad PV = rT$

or $\quad \frac{V}{T} = \frac{r}{P}$

$$\therefore \quad dS = C_P \frac{dT}{T} - \frac{r}{J} \frac{dP}{P}$$

Integrating

$$\int_{S_1}^{S_2} dS = C_P \int_{T_1}^{T_2} \frac{dT}{T} - \frac{r}{J} \int_{P_1}^{P_2} \frac{dP}{P}$$

$$S_2 - S_1 = C_P \log_e \frac{T_2}{T_1} - \frac{r}{J} \log_e \frac{P_2}{P_1} \quad \ldots(v)$$

$$S_2 - S_1 = C_P \times 2{\cdot}3026 \times \log_{10} \frac{T_2}{T_1} - \frac{r}{J} \times 2{\cdot}3026 \log_{10} \frac{P_2}{P_1} \quad \ldots(vi)$$

**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

$$S_2 - S_1 = C_P \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1} - \frac{R}{J} \times 2{\cdot}3026 \log_{10} \frac{P_2}{P_1} \quad \ldots(vii)$$

**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

$$dS = \frac{\delta H}{T}$$

$$= \frac{800}{273} = \mathbf{2{\cdot}93 \text{ cal/K}}$$



**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

$$= 5000 \times 540$$

$$= 2700000 \text{ cal}$$

$$\therefore \quad \delta H = 2700000 \text{ cal}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{2700000}{373} = \mathbf{7240 \text{ cal/K}}$$

**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 increases from −10°C to 0°C

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= ms \log_e \frac{T_2}{T_1}$$

$$= ms \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 0{\cdot}5 \times 2{\cdot}3026 \log_{10} \frac{273}{263}$$

$$= 0{\cdot}01865 \text{ cal/K}$$

(2) Increase in entropy when 1 gram of ice at 0°C is converted into water at 0°C.

$$dS = \frac{\delta H}{T}$$

$$= \frac{80}{273} = 0{\cdot}293 \text{ cal/K}$$

(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

$$dS = \frac{\delta H}{T}$$

$$= \frac{540}{373} = 1{\cdot}447 \text{ cal/K}$$

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 $= \int_{V_1}^{V_2} PdV$

But $PV = RT$

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

$$W = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$= RT \log_e \frac{V_2}{V_1}$$

Here $\frac{V_2}{V_1} = 4$

$$W = RT \times 2{\cdot}3026 \log_{10} (4)$$

Here, $W$ and $R$ are in the units of work

Gain in entropy $= \frac{\delta H}{T}$

$$= \frac{W}{JT} = \frac{RT \times 2{\cdot}3026 \log_{10} 4}{JT}$$

$$= \mathbf{1{\cdot}387 \frac{R}{J} \text{ cal/K}}$$

**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

$$= 6{\cdot}829 - 6{\cdot}023$$

$$= \mathbf{0{\cdot}806 \text{ cal/K}}$$

**Example 6·34.** *Calculate the change in entropy when 50 grams of water at 15°C is mixed with 80 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

$$= \mathbf{0{\cdot}115\ cal/K}$$

**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*)
$$m_1 = 10 \text{ g}$$
$$T_1 = 100°\text{C} = 373 \text{ K}$$
$$m_2 = 90 + 10 = 100 \text{ g}$$
$$T_2 = 273 \text{ K}$$

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

$$= \frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$
$$= 100 \int_{273}^{331{\cdot}2} \frac{dT}{T}$$



$$= 100 \times 2{\cdot}3026 \times \log_{10} \left(\frac{331{\cdot}2}{273}\right)$$
$$= +19{\cdot}32 \text{ cal/K}$$

(*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

$$= 19{\cdot}32 - 14{\cdot}47 - 1{\cdot}188$$
$$= \mathbf{+3{\cdot}662\ cal/K}$$

Hence the net increase in the entropy of the system

$$= \mathbf{3{\cdot}662\ cal/K}$$

**Example 6·36.** *1 g of water at 20°C is converted into ice at −10°C at constant pressure. Heat capacity for 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

$$dS = \frac{\delta H}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$$

$$= 1\times 2{\cdot}1\times 2{\cdot}3026\ \log_{10}\left(\frac{263}{273}\right)$$

$$= -0{\cdot}07834\ \text{J/K}$$

Total change in entropy of the system

$$= -0{\cdot}2969 - 1{\cdot}227 - 0{\cdot}07834$$

$$= \mathbf{-1{\cdot}60224\ J/K}$$

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

$$dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$$

$$= ms\times 2{\cdot}3026\ \log_{10}\frac{T_2}{T_1}$$

$$= 1000\times 1\times 2{\cdot}3026\ \log_{10}\frac{373}{273}$$

$$= \mathbf{312\ cal/K}$$

(2) (*i*) Change in entropy of the reservoir,

$$dS = \frac{-\delta H}{T}$$

$$= -\frac{1000\times 1\times 100}{373} = \mathbf{-268{\cdot}1\ cal/K}$$

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 $\delta H$ 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 $(i)$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right] - P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{dy}\right)_x dy\right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y\right] dx + \left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right] dy$$

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 $x$

$$\frac{\partial^2 U}{\partial y . \partial x} = \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y\, \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x}$$

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

$$\therefore \quad \frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial x \partial y} \text{ and}$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y \partial x} - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y \partial x}$$

$$= \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x \partial y} - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x \partial y}$$

Simplifying,

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots(iv)$$

Here $x$ and $y$ can 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 $(iv)$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(v)$$

But

$$dS = \frac{\partial H}{T}$$

$$\therefore \quad \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(vi)$$

(2) Taking $T$ and $P$ as independent variables and

$$x = T$$

and

$$y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} = 0$$

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*),

$$W \leqslant T_0 (S_2 - S_1) - (U_2 - U_1) \qquad ...(vii)$$

$$W \leqslant (U_1 - U_2) - T_0(S_1 - S_2) \qquad ...(viii)$$

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,

$$\therefore \qquad W_T \leqslant (U_1 - U_2)_T - T(S_1 - S_2)_T \qquad ...(ix)$$

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

$$(F_1 - F_2)_T = (U_1 - U_2)_T - T(S_1 - S_2)_T \qquad ...(x)$$

From (*ix*) and (*x*)

$$W_T \leqslant (F_1 - F_2)_T \qquad ...(xi)$$

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 voltaic 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 $(V_2 - V_1)$

$$\therefore \qquad \int_{V_1}^{V_2} PdV = P_0[V_2 - V_1]$$

$$\therefore \qquad W = P_0[V_2 - V_1] + A \qquad ...(i)$$

For a system that exchanges heat with a reservoir temperature

$$W \leqslant (U_1 - U_2) - T_0(S_1 - S_2) \qquad ...(ii)$$

$$P_0[V_2 - V_1] + A \leqslant (U_1 - U_2) - T_0(S_1 - S_2)$$

or

$$A \leqslant (U_1 - U_2) - T_0(S_1 - S_2) + P_0[V_1 - V_2] \qquad ...(iii)$$

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*)

$$A_{P,T} \leqslant (U_1 - U_2)_{P,T} - T(S_1 - S_2)_{P,T} + P[V_1 - V_2]_{P,T} \qquad ...(iv)$$

But, for the Gibbs function,

$$G = U - TS + PV \qquad ...(v)$$

Therefore, for two equilibrium states at the same pressure and temperature,

$$[G_1 - G_2]_{P,T} = (U_1 - U_2)_{P,T} - T[S_1 - S_2]_{P,T} + P[V_1 - V_2]_{P,T} ...(vi)$$

From equations (*iv*) and (*vi*)

$$A_{P,T} \leqslant (G_1 - G_2)_{P,T} \qquad ...(vii)$$

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

$$h = U + PV \qquad \text{...(i)}$$

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)

$$dh = dU + PdV + VdP \qquad \text{...(ii)}$$

Also

$$\delta H = dU + PdV \qquad \text{...(iii)}$$

$$\therefore \quad dh = \delta H + VdP \qquad \text{...(iv)}$$

Dividing by $dT$

$$\frac{dh}{dT} = \frac{\delta H}{dT} + V\frac{dP}{dT} \qquad \text{...(v)}$$

At constant pressure (isobaric process),

$$\left(\frac{\partial h}{\partial T}\right)_P = \left(\frac{\delta H}{dT}\right)_P$$

But $$\left(\frac{\delta H}{dT}\right)_P = C_P$$

$$\therefore \quad \left(\frac{\partial h}{\partial T}\right)_P = C_P \qquad \text{...(vi)}$$

From equation (iv), during isobaric process, $dP = 0$

$$\therefore \quad dh = \delta H$$

or $$h_f - h_i = H \qquad \text{...(vii)}$$

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 $$h_i = h_f \qquad \text{...(viii)}$$

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 $\mu$

The specific heat at constant pressure $C_P$, the specific heat at constant volume $C_V$ and the Joule-Kelvin coefficient $\mu$ are defined as follows :

$$C_P = \left(\frac{\partial h}{\partial T}\right)_P \qquad \text{...(i)}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad \text{...(ii)}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \qquad \text{...(iii)}$$

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 $\mu$ 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 Gibb's function.

Internal energy $= U$

Enthalpy, $h = U + PV$

Helmholtz function

$$F = U - TS$$

Gibb's 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 $$dU = TdS - PdV \qquad \text{...(i)}$$

Here $U$, $T$ and $P$ are supposed to be functions of $S$ and $V$

(2) The enthalpy changes by an amount

$$dh = dU + PdV + VdP$$

$$dh = (TdS - PdV) + P.dV + VdP$$

$$dh = TdS + VdP \qquad \text{...(ii)}$$

Here $h$, $T$ and $V$ are supposed to be functions of $S$ and $P$.

(3) The Helmholtz function changes by an amount

$$dF = dU - TdS - SdT$$