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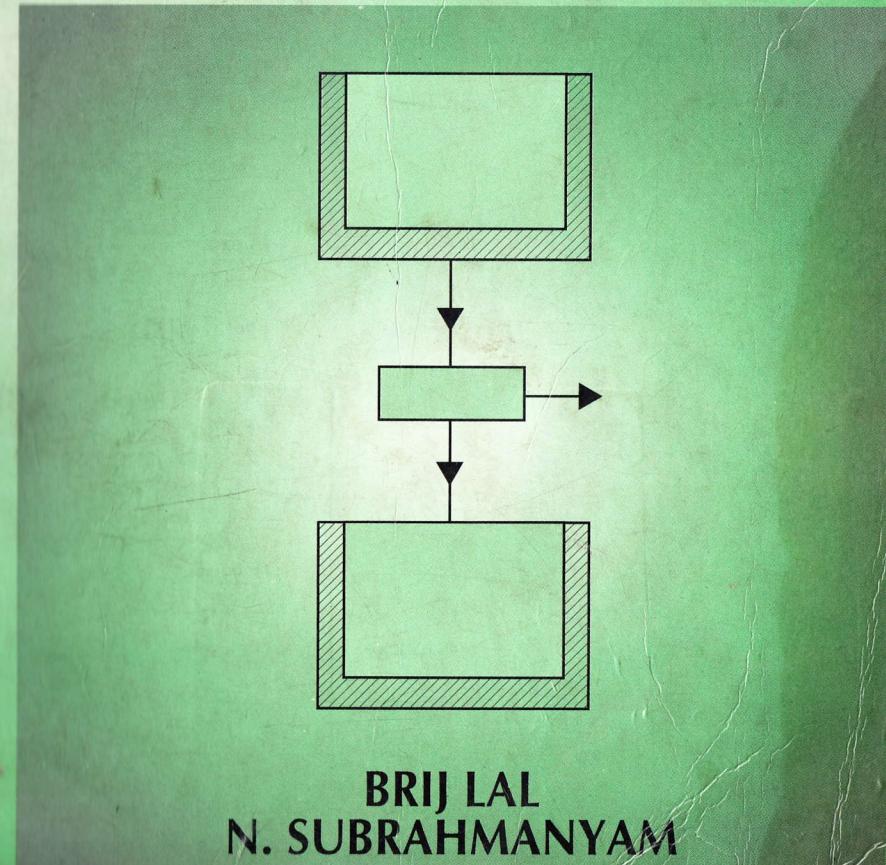
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# HEAT AND THERMODYNAMICS



**BRIJ LAL  
N. SUBRAHMANYAM**

# **HEAT AND THERMODYNAMICS**

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### 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 hard 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,

$$C_1^2 = u_1^2 + v_1^2 + w_1^2$$

### Nature of Heat ✓

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  $mu_1$ . The 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  $ADEH$ .

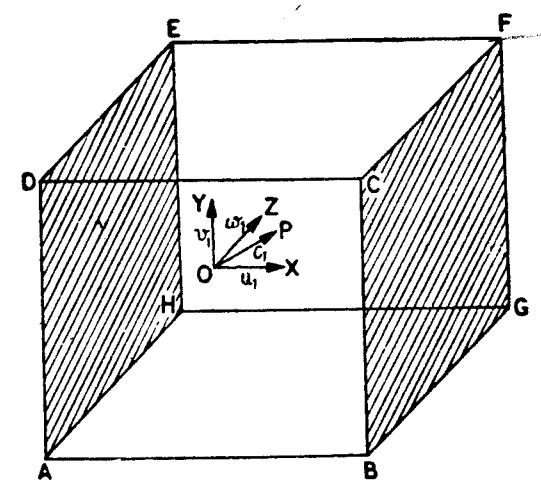


Fig. 5.7

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

$$= \frac{m}{l} [u_1^2 + u_2^2 + \dots + u_n^2]$$

Force per unit area on the wall  $BCFG$  or  $ADEH$  is equal to the pressure  $P_x$

$$P_x = \frac{m}{l \times l^2} (u_1^2 + u_2^2 + u_3^2 + \dots + u_n^2)$$

Similarly the pressure  $P_y$  on the walls  $CDEF$  and  $ABGH$  is given by

$$P_y = \frac{m}{l^3} (v_1^2 + v_2^2 + \dots + v_n^2)$$

and the pressure  $P_z$  on the walls  $ABCD$  and  $EFGH$  is given by

$$P_z = \frac{m}{l^3} (w_1^2 + w_2^2 + \dots + w_n^2)$$

As the pressure of a gas is the same in all directions, the mean pressure  $P$  is given by

$$\begin{aligned} P &= \frac{P_x + P_y + P_z}{3} \\ &= \frac{m}{3l^3} \left[ (u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) \right. \\ &\quad + (u_3^2 + v_3^2 + w_3^2) + \dots \\ &\quad \left. + (u_n^2 + v_n^2 + w_n^2) \right] \\ &= \frac{m}{3l^3} [C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2] \quad \dots(i) \end{aligned}$$

But volume,  $V = l^3$ . Let  $C$  be the root-mean-square velocity of the molecules (R.M.S. velocity).

Then

$$C^2 = \frac{C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2}{n}$$

or

$$nC^2 = C_1^2 + C_2^2 + C_3^2 + \dots + C_n^2$$

Substituting this value in equation (i), we get

$$P = \frac{m \cdot n \cdot C^2}{3V} \quad \dots(ii)$$

But  $M = mn$  where  $M$  is the mass of the gas of volume  $V$ ,  $m$  is the mass of each molecule and  $n$  is the number of molecules in a volume  $V$ .

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

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

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

From equation (iii)

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

or

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

... (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	$18.4 \times 10^4$
Helium	4	$13.1 \times 10^4$
Nitrogen	28	$4.85 \times 10^4$
Oxygen	32	$4.61 \times 10^4$
Argon	40	$4.14 \times 10^4$
Carbon dioxide	44	$3.95 \times 10^4$
Chlorine	71	$3.11 \times 10^4$

### R.M.S. velocity of hydrogen

The density of hydrogen at N.T.P. is 0.000089 g/cc. Therefore  $C$  for hydrogen can be calculated as follows :

$$\begin{aligned} C &= \sqrt{\frac{3P}{\rho}} \\ &= \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.000089}} \\ &= 1.84 \times 10^5 \text{ cm/s} \end{aligned}$$

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

$$= 16 \times 0.000089$$

$$\therefore C \text{ for oxygen} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{16 \times 0.000089}} = 4.6 \times 10^4 \text{ cm/s}$$

(c) For air the density at N.T.P. is 0.001293 g/cc

$$\therefore C \text{ for air} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001293}} = 4.850 \times 10^4 \text{ cm/s}$$

Example 5.4 Calculate the number of molecules in one c.c. of oxygen at N.T.P. using the following data :—

Density of mercury = 13.6 g/cm<sup>3</sup>

R.M.S. velocity of oxygen molecules at 0°C  
 $= 4.62 \times 10^4 \text{ cm/s}$

Mass of one molecule of oxygen =  $52.8 \times 10^{-24} \text{ g}$

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

Let the mass of each molecule be  $m$  and the number of molecules in one cc =  $n$

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

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

Here

$$P = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$m = 52.8 \times 10^{-24} \text{ g}$$

$$C = 4.62 \times 10^4 \text{ cm/s}$$

$$n = \frac{3 \times 76 \times 13.6 \times 980}{52.8 \times 10^{-24} \times (4.62 \times 10^4)^2}$$

$$n = 2.697 \times 10^{19}$$

### 5.15 Kinetic Energy per Unit Volume of a Gas

$$\begin{aligned} \text{We know } P &= \frac{1}{3} \rho C^2 \\ &= \frac{2}{3} \cdot \frac{1}{2} \rho C^2 \\ &= \frac{2}{3} \cdot E \end{aligned}$$

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

$$PV = RT$$

$$\therefore \frac{1}{3} MC^2 = RT$$

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

... (i)

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

$$M = m \times N$$

$$\frac{1}{2} mNC^2 = \frac{3}{2} RT$$

$$\begin{aligned} \frac{1}{2} mC^2 &= \frac{3}{2} \frac{R}{N} T \\ &= \frac{3}{2} k T \end{aligned}$$

... (ii)

Here  $k$  is called Boltzmann's constant.  $(O b(1))$  and  $C$

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.

$\checkmark$  Example 5.5 At what celsius temperature will oxygen molecules have the same root mean square velocity as that of hydrogen molecules at  $-100^\circ\text{C}$ ?

The energy of a gas molecule is,

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

For hydrogen molecules

$$\frac{1}{2} m_1 C_1^2 = \frac{3}{2} kT_1$$

For oxygen molecules

$$\frac{1}{2} m_2 C_2^2 = \frac{3}{2} kT_2$$

Dividing (i) by (ii)

$$\frac{m_1 C_1^2}{m_2 C_2^2} = \frac{T_1}{T_2}$$

Here

$$C_1 = C_2$$

$$\begin{aligned} T_1 &= -100^\circ\text{C} \\ &= -100 + 273 \end{aligned}$$

$$\begin{aligned} &= 173 \text{ K} \\ T_3 &=? \\ \frac{m_2}{m_1} &= 16 \end{aligned}$$

From equation (iii)

$$T_2 = \frac{m_2 C_2^2 T_1}{m_1 C_1^2}$$

$$\begin{aligned} T_2 &= 16 \times 173 \\ &= 2768 \text{ K} \\ T_2 &= 2768 - 273 \\ &= 2495^\circ\text{C} \end{aligned}$$

**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.

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

$$\text{Here } P = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$\rho = 16 \times 0.000089$$

$$\therefore C = \sqrt{\frac{3 \times 76 \times 13.6 \times 980}{16 \times 0.000089}}$$

$$C = 4.6 \times 10^4 \text{ cm/s}$$

Let the RMS velocity of the molecules at 27°C be  $C_1$

$$\therefore \frac{C_1}{C} = \sqrt{\frac{T_1}{T}}$$

$$C_1 = C \times \sqrt{\frac{T_1}{T}}$$

$$\text{Here } C = 4.6 \times 10^4 \text{ cm/s}$$

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

$$T_1 = 27^\circ\text{C}$$

$$= 27 + 273$$

$$= 300 \text{ K}$$

$$C_1 = 4.6 \times 10^4 \sqrt{\frac{300}{273}}$$

$$C_1 = 4.84 \times 10^4 \text{ cm/s}$$

### 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

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

$$= \frac{1}{2} NmC^2$$

$$\therefore PV = \frac{1}{3} NmC^2$$

$$= \frac{2}{3} N \cdot \frac{1}{2} mC^2$$

Mean kinetic energy of a molecule

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

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

$$\therefore PV = \frac{2}{3} N \cdot \frac{3}{2} kT$$

$$PV = NkT$$

$$\text{But } N \times k = R$$

$$\therefore PV = RT$$

... (ii)

Note on the Gas Equation.

In the gas equation

$$PV = RT$$

$P$  is in dynes/sq cm

$$R = 8.31 \times 10^7 \text{ ergs/g mol-K}$$

$T$  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

$$P = 76 \times 13.6 \times 980 \text{ dynes/sq cm}$$

$$T = 27 + 273$$

$$= 300 \text{ K}$$

$$R = 8.31 \times 10^7 \text{ ergs/g mol-K}$$

$$PV = RT$$

$$V = \frac{8.31 \times 10^7 \times 300}{76 \times 13.6 \times 980} \text{ cc per g-mol}$$

$$V = 24610 \text{ cc per g mol}$$

$$\begin{aligned} \text{Volume for } 3.2 \text{ g of oxygen} &= v \\ &= \frac{24610 \times 3.2}{32} \\ &= 2461 \text{ cc} \end{aligned}$$

### 5.18. Derivation of Gas Laws

#### (i) Boyle's Law

According to the kinetic theory,

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

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

$$PV = \frac{1}{3} MC^2 \quad \dots(i)$$

At a constant temperature  $T$ ,  $C^2$  is constant. Therefore at a constant temperature

$$\frac{1}{3} MC^2 = \text{constant}$$

Hence  $PV = \text{const.} \rightarrow \text{at constant temperature.}$

#### (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  $T$ .

$$M = mN$$

$$PV = \frac{1}{3} NmC^2 \quad \dots(i)$$

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),

$$PV = NkT \quad \dots(ii)$$

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

If  $P$  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.

*10 d end*

#### (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,

$$PV = RT$$

$$\text{But } R = Nk$$

$$PV = NkT.$$

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

$$P = nkT$$

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

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

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

**Example 5.9.** Calculate the number of molecules in one cubic metre of an ideal gas at N.T.P.

Let the number of molecules per cc be  $n$ .

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

Number of molecules in one cubic metre volume

$$x = n \times 10^6$$

$$x = \frac{PN \times 10^6}{RT}$$

Here

$$P = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$N = 6.023 \times 10^{23}$$

$$R = 8.31 \times 10^7 \text{ erg/g mol-K}$$

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

$$x = \frac{76 \times 13.6 \times 980 \times 6.023 \times 10^{23} \times 10^6}{8.31 \times 10^7 \times 273}$$

$$x = 2.688 \times 10^{25}$$

**Example 5.10** Calculate the number of molecules in one litre of an ideal gas at 136.5°C temperature and 3 atmospheres 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

$$P = 3 \times 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$N = 6.023 \times 10^{23}$$

$$R = 8.31 \times 10^7 \text{ ergs/g mol-K}$$

$$T = (273 + 136.5)$$

$$= 409.5 \text{ K}$$

$$\therefore x = \frac{3 \times 76 \times 13.6 \times 980 \times 6.023 \times 10^{23} \times 10^6}{8.31 \times 10^7 \times 409.5}$$

$$x = 5.376 \times 10^{22}$$

**Example 5.11** The number of molecules per cc of a gas is  $2.7 \times 10^{23}$  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.

$$P_1 = \frac{1}{3} mn_1 C^2 \quad \dots (i)$$

At 0°C and  $10^{-6}$  mm pressure

$$P_2 = \frac{1}{3} mn_2 C^2 \quad \dots (ii)$$

From (i) and (ii)

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$n_2 = \frac{n_1 \times P_2}{P_1}$$

or

Here

$$n_1 = 2.7 \times 10^{23}$$

$$P_1 = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$P_2 = 10^{-6} \text{ mm of Hg}$$

$$= 10^{-7} \text{ cm of Hg}$$

$$P_2 = 10^{-7} \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$n_2 = \frac{2.7 \times 10^{23} \times 10^{-7} \times 13.6 \times 980}{76 \times 13.6 \times 980}$$

$$n_2 = 3.553 \times 10^{10}$$

(ii) Let the R.M.S. velocity at 0°C be  $C_1$  and at 39°C be  $C_2$ . Number of molecules per cc at 0°C and  $10^{-6}$  mm of Hg pressure

$$= n_1$$

and at 39°C and  $10^{-6}$  mm of Hg pressure

$$= n_2$$

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

Here pressure is the same in both the cases

$$\therefore \frac{1}{3} mn_1 C_1^2 = \frac{1}{3} mn_2 C_2^2$$

$$\therefore n_2 C_1^2 = n_1 C_2^2$$

$$n_2 = n_1 \frac{C_2^2}{C_1^2}$$

But

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

$$\frac{C_2^2}{C_1^2} = \frac{T_2}{T_1}$$

$$\therefore n_2 = \frac{n_1 \times T_2}{T_1}$$

Here

$$n_1 = 3.553 \times 10^{10}$$

$$T_1 = 0^\circ \text{ C}$$

$$= 273 \text{ K}$$

$$T_2 = 39^\circ \text{ C}$$

$$= 273 + 39$$

$$= 312 \text{ K}$$

$$\therefore n_2 = \frac{3.553 \times 10^{10} \times 273}{312}$$

$$n_2 = 3.109 \times 10^{10}$$

### 5.19 Avogadro's Hypothesis

Consider two gases A and B at a pressure  $P$  and each having a volume  $V$ .

Mass of each molecule of the first gas =  $m_1$

Number of molecules of the first gas =  $n_1$

Mean square velocity of the molecules of the first gas =  $C_1^2$   
For the first gas

$$P = \frac{1}{3} \rho_1 C_1^2 \\ = \frac{1}{3} \frac{m_1 n_1 C_1^2}{V} \quad \dots(i)$$

Similarly for the second gas

$$P = \frac{1}{3} \rho_2 C_2^2 \\ = \frac{1}{3} \frac{m_2 n_2 C_2^2}{V} \quad \dots(ii)$$

where  $m_2$  represents the mass of each molecule,  $n_2$  the number of molecules and  $C_2^2$  the mean square velocity of the molecules.

From (i) and (ii),

$$\frac{1}{3} \frac{m_1 n_1 C_1^2}{V} = \frac{1}{3} \frac{m_2 n_2 C_2^2}{V}$$

or

$$m_1 n_1 C_1^2 = m_2 n_2 C_2^2 \quad \dots(iii)$$

If the two gases are at the same temperature  $T$ , the mean kinetic energy of the molecules of both the gases is the same

$$\frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2$$

$$\therefore m_1 C_1^2 = m_2 C_2^2$$

From (iii) and (iv),  $\Delta (O \text{ d end}) \quad \dots(iv)$

$$n_1 = n_2$$

Hence, equal volumes of all gases under similar conditions of temperature and pressure have the same number of molecules. This represents Avogadro's hypothesis.

### 5.20 Graham's Law of Diffusion of Gases

According to the kinetic theory

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

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

$$C \propto \frac{1}{\sqrt{\rho}}$$

It means that the root mean square velocity of the molecules of a gas is inversely proportional to the square root of its density. Consider two gases whose root mean square velocities are  $C_1$  and  $C_2$ .

$$\frac{C_1}{C_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}}$$

or

### Nature of Heat

Here,  $r_1$  and  $r_2$  represent the rates of diffusion of the two gases.

**Example 5.12.** Calculate the total random kinetic energy of one gm-molecule of oxygen at 300 K.

Total random kinetic energy per gram-molecule of oxygen

$$= \frac{1}{2} m C^2 \times N \\ = \frac{3}{2} k T \cdot N \\ = \frac{3}{2} \cdot \frac{R}{N} T \cdot N \\ = \frac{3}{2} R T \\ = \frac{3}{2} \times 8.3 \times 10^7 \times 300 \\ = 3.735 \times 10^{10} \text{ ergs} \\ = 3735 \text{ joules}$$

**Note.** The total random kinetic energy for one gram-molecule of any gas i.e., hydrogen, oxygen, helium, nitrogen, air etc. is the same at the same temperature.

**Example 5.13.** Calculate the average kinetic energy of a molecule of a gas at a temperature of 300 K.

Average K.E. of a molecule

$$= \frac{1}{2} m C^2 = \frac{3}{2} k T$$

Here  $k$  is Boltzmann's constant.

$$k = 1.38 \times 10^{-16} \text{ erg/molecule-deg}$$

$$\text{Average K.E. of a molecule} = \frac{3}{2} \times 1.38 \times 10^{-16} \times 300 \\ = 6.21 \times 10^{-14} \text{ ergs}$$

**Note.** The average kinetic energy of a molecule of any gas i.e., hydrogen, oxygen, helium, nitrogen, air, etc., is the same at the same temperature.

**Example 5.14.** Calculate the mean translational kinetic energy per molecule of a gas at 727°C, given  $R = 8.32$  joules/mole-K.

(Delhi, 1974)

Avogadro's number,

$$N = 6.06 \times 10^{23}$$

$$T = 627 + 273 = 1000 \text{ K}$$

$$R = 8.32 \text{ joules/mol-K}$$

$$N = 6.06 \times 10^{23}$$

$$k = \frac{R}{N} = \left( \frac{8.32}{6.06 \times 10^{23}} \right) \text{ joules/molecule-K}$$

$$\text{Mean translational kinetic energy per molecule} = \frac{3}{2} k T$$

Here

$$= \frac{3 \times 8.32 \times 1000}{2 \times 6.06 \times 10^{23}} \\ = 2.059 \times 10^{-20} \text{ joule}$$

**Example 5.15.** Calculate the total random kinetic energy of one gram of nitrogen at 300 K.

Total random energy for one gram molecule of nitrogen

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

Total random energy for 1 gram of nitrogen

$$= \frac{3 RT}{2 M}$$

where the molecular weight of nitrogen  $M = 28$  g

$$E = \frac{3RT}{2M} \\ = \frac{3 \times 8.3 \times 10^7 \times 300}{2 \times 28} \\ = 133.4 \times 10^7 \text{ ergs} \\ = 133.4 \text{ joule}$$

**Note.** The total random kinetic energy for 1 gram of a gas is different for different gases at the same temperature.

**Example 5.16.** Calculate the total random kinetic energy of 2 g of helium at 200 K.

Energy for 1 g of helium

$$= \frac{3RT}{2M}$$

Energy for 2 g of helium

$$= \frac{2 \times 3 \times RT}{2M} \\ = \frac{3RT}{M} \\ = \frac{3 \times 8.3 \times 10^7 \times 200}{4} \\ = 1245 \times 10^7 \text{ ergs} \\ = 1245 \text{ joules}$$

**Example 5.17.** Calculate the root mean square velocity of a molecule of mercury vapour at 300 K.

Mean kinetic energy of one molecule of mercury

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

Let  $N$  be the Avogadro's number.

$$\text{Then } \frac{1}{2} mNC^2 = \frac{3}{2} kNT$$

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

$$C = \sqrt{\frac{3RT}{M}}$$

Here the molecular weight of mercury,  $M = 221$

$$\therefore C = \sqrt{\frac{3 \times 8.3 \times 10^7 \times 300}{221}} \\ = 1.93 \times 10^4 \text{ cm/s}$$

**Example 5.18.** With what speed would one gram molecule of oxygen at 300 K be moving in order that the translational kinetic energy of its centre of mass is equal to the total random kinetic energy of all its molecules? Molecular weight of oxygen ( $M$ ) = 32.

Total random kinetic energy of 1 gram-molecule of oxygen

$$= \frac{3}{2} RT = \frac{3}{2} \times 8.3 \times 10^7 \times 300 \\ = 3.735 \times 10^{10} \text{ ergs}$$

Kinetic energy of  $M$  grams of oxygen moving with a velocity  $v$

$$= \frac{1}{2} Mv^2 \\ \therefore \frac{1}{2} Mv^2 = 3.735 \times 10^{10} \\ \frac{1}{2} \times 32 \times v^2 = 3.735 \times 10^{10} \\ v^2 = \frac{3.735 \times 10^{10}}{16} \\ v = 4.8 \times 10^4 \text{ cm/s}$$

**Example 5.19.** Calculate the temperature at which the r.m.s. velocity of a hydrogen molecule will be equal to the speed of the earth's first satellite (i.e.  $v = 8 \text{ km/s}$ ).

Energy for 1 gram molecule of hydrogen

$$= \frac{1}{2} Mv^2 = \frac{3}{2} RT \\ T = \frac{Mv^2}{3R} \\ = \frac{2 \times (8 \times 10^5)^2}{3 \times 8.3 \times 10^7} \\ = 5.14 \times 10^3 \text{ K}$$

**Example 5.20.** At what temperature, pressure remaining constant, will the r.m.s. velocity of a gas be half its value at 0°C?

[Delhi (Hons.) 1975]

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

Here

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

$$T_2 = ?$$

$$T_1 = 273 \text{ K}$$

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

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

$$T_2 = \frac{273}{4} = 68.25 \text{ K}$$

$$T_2 = -204.75^\circ\text{C}$$

or

### 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

$$\frac{1}{2} m C^2 = \frac{3}{2} kT \quad \dots(i)$$

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

$$\therefore u^2 = v^2 = w^2$$

or

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

$$\begin{aligned} \therefore \frac{1}{2} m C^2 &= 3 [\frac{1}{2} m(u^2)] = 3 [\frac{1}{2} m(v^2)] \\ &= 3 [\frac{1}{2} m(w^2)] \\ &= \frac{3}{2} kT \end{aligned}$$

$$\begin{aligned} \therefore \frac{1}{2} m u^2 &= \frac{1}{2} kT & \dots(ii) \\ \frac{1}{2} m v^2 &= \frac{1}{2} kT & \dots(iii) \\ \frac{1}{2} m w^2 &= \frac{1}{2} kT & \dots(iv) \end{aligned}$$

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. ~~✓~~ End

### 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.

$$\text{Energy associated with each degree of freedom} = \frac{1}{2} kT$$

$$\text{Energy associated with three degrees of freedom}$$

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

Consider one gram molecule of a gas.

Energy associated with one gram molecule of a gas

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

$$= \frac{3}{2} (N \times k) T$$

$$[\text{But, } N \times k = R]$$

$$U = \frac{3}{2} RT$$

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.

$$\therefore C_v = \frac{dU}{dT} = \frac{3}{2} R$$

$\left( \frac{dU}{dT} \right)$  is the increase in internal energy per unit degree rise of temperature )

$$\text{But } C_p - C_v = R$$

$$C_p = C_v + R$$

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

For a mono-atomic gas

$$\begin{aligned} \gamma &= \frac{C_p}{C_v} \\ &= \frac{\frac{5}{2} R}{\frac{3}{2} R} = 1.67 \end{aligned}$$

The value of  $\gamma$  is found to be true experimentally for monoatomic gases like argon and helium.

**10.1 (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  $C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{5}{2} R + R = \frac{7}{2} R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{\frac{7}{2} R}{\frac{5}{2} R} = 1.40$$

10.8 (End)

The value of  $\gamma = 1.40$  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

$$C_P - C_V = R$$

$$C_P = C_V + R$$

$$= 3R + R = 4R$$

$$\begin{aligned}\gamma &= \frac{C_P}{C_V} \\ &= \frac{4R}{3R} = 1.33\end{aligned}$$

(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  $C_P - C_V = R$

$$C_P = C_V + R$$

$$= \frac{7}{2} R + R = \frac{9}{2} R$$

$$\gamma = \frac{C_P}{C_V}$$

$$= \frac{9/2 R}{7/2 R} = 1.28$$

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

end of the plate. After a short time, sufficient quantity of silver is deposited on the plate  $P$ . Using a spectro-photometer, the relative

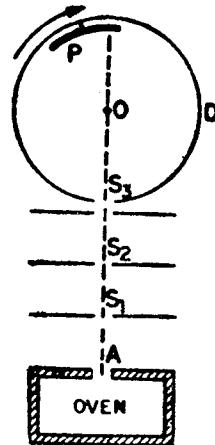


Fig. 5-9

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

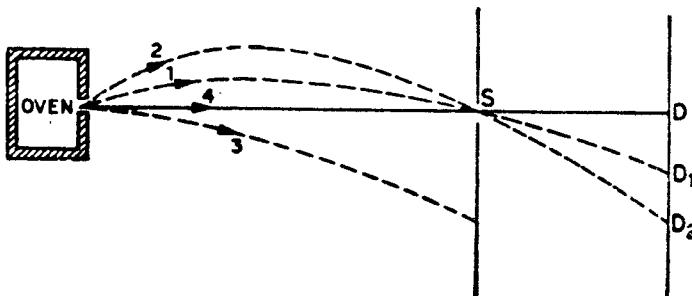


Fig. 5-10

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.

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*The distance travelled by a molecule between two consecutive collisions is called mean free path.*

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

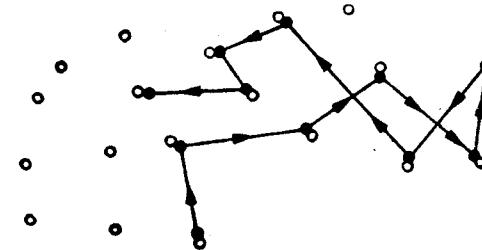


Fig. 5-11

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

$$\lambda = \frac{S}{N} \quad \dots (i)$$

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 (1), corresponds to the volume of a cylinder of diameter  $2d$  as (2).

(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 =  $\pi d^2 v \times n$ .

$$\therefore \text{Mean free path } \lambda = \frac{v}{\pi d^2 v n} \\ = \frac{1}{\pi d^2 n} \quad \dots(i)$$

This equation was deduced by Clausius.

$$\therefore \lambda \propto \frac{1}{d^2} \quad \dots(ii)$$

The mean free path is inversely proportional to the square of the diameter of the molecules.

Let  $m$  be the mass of each molecule.

Then,  $m \times n = \rho$   
 $\lambda = \frac{m}{\pi d^2 \rho} \quad \dots(iii)$

The mean free path is inversely proportional to the density of the gas.

The expression for the mean path according to Boltzmann is

$$\lambda = \frac{3}{4\pi d^2 n} \quad \dots(iv)$$

He assumed that all molecules have the same average speed.

Maxwell derived the expression,

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

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	$2.47 \times 10^{-8}$ cm	$1.83 \times 10^{-6}$ cm
Nitrogen	$3.50 \times 10^{-8}$ cm	$0.944 \times 10^{-6}$ cm
Helium	$2.18 \times 10^{-8}$ cm	$2.85 \times 10^{-6}$ cm
Oxygen	$3.39 \times 10^{-8}$ cm	$0.909 \times 10^{-6}$ 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,

$$mn = \rho$$

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

$$\lambda = \frac{3\eta}{\rho C} \quad \dots(i)$$

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

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

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

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

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

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

Equation (iii) has to be modified in case the gas as a whole possesses mass motion.

Let  $u_0$ ,  $v_0$  and  $w_0$  be the components of the mass velocity. Therefore, the actual velocity of a molecule consists of two parts :

(i) the mass velocity components  $u_0$ ,  $v_0$  and  $w_0$

(ii) the random thermal velocity components

$$u - u_0, v - v_0 \text{ and } w - w_0$$

Corresponding to thermal motion without mass motion, similar quantities with mass motion are

$$U = u - u_0$$

$$V = v - v_0$$

and

$$W = w - w_0$$

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

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

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.

$$= N \times 3kT = 3RT$$

$$U = 3RT$$

$$A_H = \frac{dU}{dT}$$

$$= 3R = 5.96 \text{ cals/g-mole K}$$

Thus, the atomic heat of solids ( $A_H$ ) is  $3R$  and this value agrees with the Dulong and Petit's Law.

**Example 5.21.** In an experiment, the viscosity of the gas was found to be  $1.66 \times 10^{-4}$  dynes/cm<sup>2</sup> per unit velocity gradient. The R.M.S. velocity of the molecules is  $4.5 \times 10^4$  cm/s. The density of the gas is 1.25 grams per litre.

Calculate (i) the mean free path of the molecules of the gas, (ii) frequency of collision and (iii) molecular diameter of the gas molecules.

Here

$$\eta = 1.66 \times 10^{-4} \text{ units}$$

$$C = 4.5 \times 10^4 \text{ cm/s}$$

$$\rho = 1.25 \times 10^{-3} \text{ g/cc}$$

$$(i) \lambda = \frac{3\eta}{\rho C}$$

$$\lambda = \frac{3 \times 1.66 \times 10^{-4}}{1.25 \times 10^{-3} \times 4.5 \times 10^4}$$

$$\lambda = 9 \times 10^{-8} \text{ cm}$$

(ii) Frequency of collision = number of collisions per second

$$= \frac{\text{R.M.S. velocity}}{\text{Mean free path}}$$

$$\therefore N = \frac{C}{\lambda}$$

$$N = \frac{4.5 \times 10^4}{9 \times 10^{-8}}$$

$$N = 5 \times 10^{11}$$

(iii) Avogadro's number

$$= 6.023 \times 10^{23}$$

Number of molecules per cc =  $n$

$$= \frac{6.023 \times 10^{23}}{22400}$$

According to Maxwell's relation

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

$$\therefore d = \frac{1}{\sqrt{1.414 \times \pi \times n \times \lambda}}$$

$$d = \frac{1}{\sqrt{1.414 \times 3.142 \times \left( \frac{6.023 \times 10^{23}}{22400} \right) \times 9 \times 10^{-8}}} \\ d = 3 \times 10^{-8} \text{ cm}$$

**Example 5.22.** In an experiment the viscosity of the gas was found to be  $2.25 \times 10^{-4}$  CGS units. The R.M.S. velocity of the molecules is  $4.5 \times 10^4$  cm/s. The density of the gas is 1 gram per litre. Calculate the mean free path of the molecules.

Here

$$\eta = 2.25 \times 10^{-4} \text{ CGS units}$$

$$C = 4.5 \times 10^4 \text{ cm/s}$$

$$\rho = 1 \text{ g/litre}$$

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

∴

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

$$\lambda = \frac{3 \times 2.25 \times 10^{-4}}{10^{-3} \times 4.5 \times 10^4}$$

$$\lambda = 15 \times 10^{-8} \text{ cm}$$

**Example 5.23.** Calculate the mean free path of a gas molecule, given that the molecular diameter is  $2 \times 10^{-8}$  cm and the number of molecule per cc is  $3 \times 10^{19}$ .

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

$$= \frac{1}{3.14 \times (2 \times 10^{-8})^2 \times 3 \times 10^{19}} \\ \lambda = 3 \times 10^{-5} \text{ cm}$$

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

**Example 5.24.** Calculate the mean free path of gas molecules in a chamber of  $10^{-6}$  mm of mercury pressure, assuming the molecular diameter to be  $2 \text{ \AA}$ . One gram molecule of the gas occupies 22.4 litres at N.T.P. Take the temperature of the chamber to be 273 K. (Agra 1975)

At 760 mm Hg pressure and 273 K temperature, the number of molecules in 22.4 litres of a gas  
 $= 6.023 \times 10^{23}$

Therefore, the number of molecules per  $\text{cm}^3$  in the chamber at  $10^{-6}$  mm pressure and 273 K temperature

$$n = \frac{6.023 \times 10^{23} \times 10^{-3}}{22400 \times 760}$$

$$n = 3.538 \times 10^{10} \text{ molecules/cm}^3$$

$$d = 2 \text{ \AA} = 2 \times 10^{-8} \text{ cm}$$

Mean free path,

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

$$= \frac{1}{3.14 \times (2 \times 10^{-8})^2 \times 3.538 \times 10^{10}} = 2.25 \times 10^4 \text{ cm}$$

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

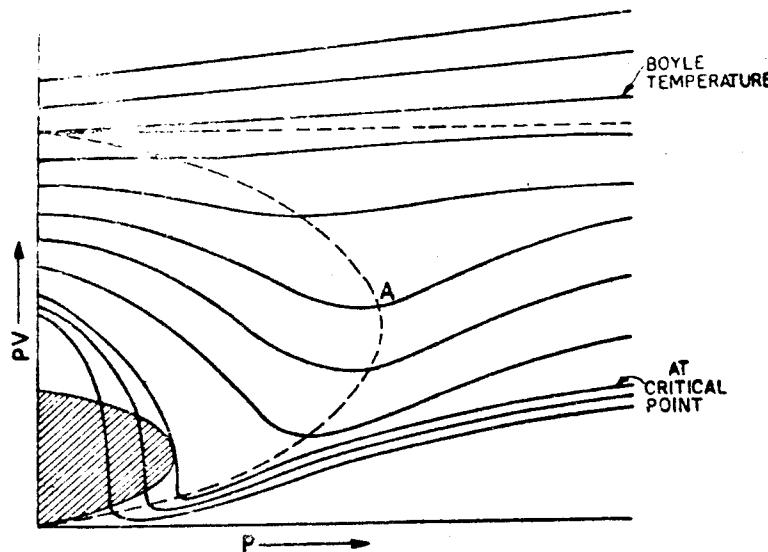


Fig. 5.18.

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 perfect 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.

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

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

approximate -  $\frac{1}{V^2} = \frac{1}{V_0^2} \cdot \frac{V_0^2}{V^2} = \frac{1}{V_0^2} \cdot \frac{V_0^2}{(V_0 + \frac{S}{n})^2} = \frac{1}{V_0^2} \cdot \frac{V_0^2}{V_0^2 + 2V_0 \cdot \frac{S}{n} + (\frac{S}{n})^2} = \frac{1}{V_0^2} \cdot \frac{V_0^2}{V_0^2 + 2V_0 \cdot \frac{S}{n}} = \frac{1}{V_0^2} \cdot \frac{V_0^2}{V_0^2 + \frac{2nS}{V_0}}$

### Nature of Heat

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

$$= \frac{V+(V-S)+(V-2S)+\dots+(V-(n-1)S)}{n}$$

$$= V - \frac{S}{n} \{ 1+2+3+\dots+(n-1) \}$$

$$= V - \frac{S}{n} \cdot \frac{(n-1)n}{2}$$

$$= V - \frac{nS}{2} + \frac{S}{2}$$

As the number of molecules is very large  $\frac{S}{2}$  can be neglected.

$\therefore$  Average space available for each molecule

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

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

$$= V - 4(nx)$$

$$= V - b$$

$\therefore b = 4(nx) = \text{four times the actual volume of the molecules}$

Thus the Van der Waals equation of state for a gas is

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

where  $a$  and  $b$  are Van der Waals constants.

From the Van der Waals equation of state

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

$$P = \frac{RT}{V - b - \frac{a}{V^2}} \quad \dots(ii)$$

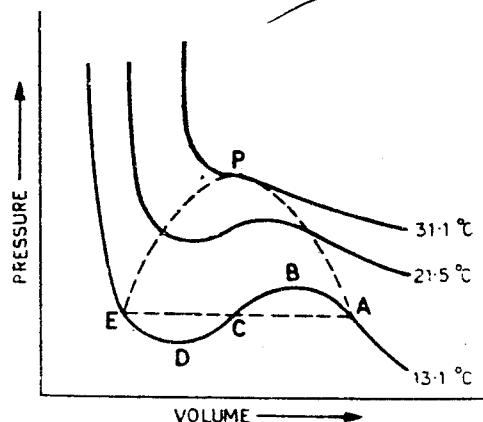


Fig. 5.19

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  $\text{CO}_2$  as obtained by Andrews. However, the portion AB has been explained as due to supercooling of the vapours and the portion ED due to super-heating of the liquid. But the portion BCD cannot be explained because it shows decrease in volume with

decrease in pressure. It is not possible in actual practice. The states AB and ED, though unstable, can be realized in practice by careful experimentation. At higher temperatures, the theoretical and experimental isothermals are similar.

Until now as many as 56 different equations of state have been suggested. But no single equation satisfies all the observed facts.

Dicterice (1901) has suggested an equation

$$P(V - b) = RT e^{-\frac{a}{RTV}}$$

Berthelot has suggested an equation

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

### 5.37 Critical Constants

(D) 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 called the point of inflexion.

According to Van der Waals equation

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

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

Differentiating  $P$  with respect to  $V$

$$\frac{dP}{dV} = \frac{-RT}{(V - b)^2} + \frac{2a}{V^3} \quad \dots(iii)$$

At the critical point  $\frac{dP}{dV} = 0$

$$T = T_c$$

$$V = V_c$$

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

$$\text{or} \quad \frac{2a}{V_c^3} = \frac{RT_c}{(V_c - b)^2} \quad \dots(iv)$$

Differentiating equation (iii)

$$\frac{d^2P}{dV^2} = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4}$$

At the critical point  $\frac{d^2P}{dV^2} = 0$ ,

$$T = T_c$$

$$V = V_c$$

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

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

Dividing (iv) by (v)

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

or

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

$$V_c = 3b \quad \dots(vi)$$

Substituting the value of

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

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

or

$$T_c = \frac{8a}{27Rb} \quad \dots(vii)$$

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

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

$$P_c = \frac{a}{27b^2} \quad \text{Ans} \quad \dots(viii)$$

### 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

$$\frac{P_1}{P_{c1}} = \frac{P_2}{P_{c2}}$$

$$\frac{V_1}{V_{c1}} = \frac{V_2}{V_{c2}}$$

$$\frac{T_1}{T_{c1}} = \frac{T_2}{T_{c2}}$$

and

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

Given  $V_c = 3b \quad \dots(i)$

$$P_c = \frac{a}{27b^2} \quad \dots(ii)$$

$$T_c = \frac{8a}{27Rb} \quad \dots(iii)$$

From equations (iii) and (ii)

$$\begin{aligned} \frac{T_c^2}{P_c} &= \frac{64a^2}{(27)^2 R^2 b^2} \times \frac{27b^2}{a} \\ &= \frac{64a}{27R^2} \\ \therefore a &= \frac{27}{64} \frac{R^2 T_c^2}{P_c} \quad \dots(iv) \end{aligned}$$

Dividing (iii) by (ii)

$$\begin{aligned} \frac{T_c}{P_c} &= \frac{8a}{27Rb} \times \frac{27b^2}{a} \\ &= \frac{8b}{R} \\ b &= \frac{RT_c}{8P_c} \quad \dots(v) \end{aligned}$$

Also

$$\frac{RT_e}{P_e V_e} = \frac{R(8a) \cdot 27b^2}{27 Rb \alpha (3b)}$$

$$\frac{RT_e}{P_e V_e} = \frac{8}{3} \quad \} \quad \dots(vi)$$

The quantity  $\frac{RT_e}{P_e V_e}$  is called the *critical coefficient* of a gas.

Its calculated value =  $\frac{8}{3}$  and it is the same for all gases.  $\checkmark$   $\checkmark$   $\checkmark$

The experimental values of the critical coefficient for different gases is given below.

TABLE

**Experimental Values of Critical Coefficient  $\frac{RT_e}{P_e V_e}$**

Substance	$T_e$ in K	$P_e$ in atm.	Specific volume in $\text{cm}^3/\text{g}$	$\frac{RT_e}{P_e V_e}$
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  $V_c = \text{molecular wt} \times \text{specific volume}$ .

The experimental value of the critical coefficient of all gases is greater than the theoretical value of 2.67.

**Example 5.24.** Calculate the Van der Waals constants for dry air, given that

$$T_e = 132 \text{ K}, P_e = 37.2 \text{ atmospheres},$$

$$R \text{ per mole} = 82.07 \text{ cm}^3 \text{ atmos K}^{-1}. \quad (\text{Delhi 1975})$$

$$\text{Here } P_e = 37.2 \text{ atmospheres}$$

$$T_e = 132 \text{ K}$$

$$R = 82.07 \text{ cm}^3 \text{ atmos K}^{-1}$$

$$(i) \quad a = \frac{27}{64} \frac{R^2 T_e^2}{P_e}$$

$$a = \left( \frac{27}{64} \right) \frac{(82.07)^2 (132)^2}{37.2}$$

$$a = 13.31 \times 10^{-6} \text{ atmos cm}^6$$

or

(ii)

$$b = \frac{RT_e}{8P_e}$$

$$b = \frac{82.07 \times 132}{8 \times 37.2}$$

or

$$b = 36.41 \text{ cm}^3$$

**5.40 Reduced Equation of State**

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

$$\frac{P}{P_e} = \alpha, \frac{V}{V_e} = \beta, \frac{T}{T_e} = \gamma$$

$$P = \alpha P_e, V = \beta V_e, T = \gamma T_e$$

According to Van der Waals equation

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

$$\text{or } \left( \alpha P_e + \frac{a}{\beta^2 V_e^2} \right) (\beta V_e - b) = R \gamma T_e$$

$$\text{But } P_e = \frac{a}{27 b^2}$$

$$V_e = 3b$$

$$\text{and } T_e = \frac{8a}{27 Rb}$$

$$\therefore \left[ \frac{\alpha \cdot a}{27 b^2} + \frac{a}{\beta^2 9b^2} \right] [\beta \cdot 3b - b] = \frac{R \gamma 8a}{27 Rb}$$

$$\left[ \alpha + \frac{3}{\beta^2} \right] [3\beta - 1] = 8\gamma \quad \dots(ii)$$

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.

its centre of mass is equal to the total random kinetic energy of all its molecules? (Molecular weight of hydrogen = 2)

[Ans.  $1.93 \times 10^6$  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.  $10.28 \times 10^3$  K]

62. Calculate the mean kinetic energy of a molecule of a gas at  $1,000^\circ\text{C}$ . Given,

$$R = 8.31 \times 10^7 \text{ ergs/gram mol-K}$$

$$N = 6.02 \times 10^{23}$$

(Delhi 1969) [Ans.  $2.07 \times 10^{-13}$  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.  $4.95 \times 10^4$  cm/s]

64. At what temperature is the R.M.S. speed of oxygen molecules twice their R.M.S. speed at  $27^\circ\text{C}$ ? (Delhi 1973) [Ans.  $927^\circ\text{C}$ ]

65. Calculate the R.M.S. velocity of the molecules of hydrogen at  $0^\circ\text{C}$ . Molecular weight of hydrogen = 2.016 and

$$R = 8.31 \times 10^7 \text{ ergs/gram mole } ^\circ\text{C}$$

(Delhi 1971) [Ans.  $18.4 \times 10^4$  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.  $1.88 \times 10^6$  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) Halberon'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.

## 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 :

$\checkmark$  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

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B)$$

$$\text{or } F_1[P_A, V_A, P_B, V_B] = 0 \quad \dots(i)$$

Expression (i) can be solved, and

$$P_B = f_1[P_A, V_A, V_B] \quad \dots(ii)$$

If  $B$  and  $C$  are in thermal equilibrium

$$\phi_2(P_B, V_B) = \phi_3(P_C, V_C)$$

$$\text{or } F_2[P_B, V_B, P_C, V_C] = 0$$

$$\text{Also } P_B = f_2[V_B, P_C, V_C] \quad \dots(iii)$$

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

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

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.

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

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

$$\phi_1(P_A, V_A) = \phi_3(P_C, V_C) \quad \dots(vi)$$

In general,

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) \quad \dots(vii)$$

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.

$$\therefore \phi(P, V) = T \quad \dots(viii)$$

This is called the equation of state of the fluid.  $\checkmark$

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  $A$ ,

$$H = U_2 - U_1 + W \quad \dots(i)$$

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  $B$ ,

$$H' = U_2' - U_1' + W' \quad \dots(ii)$$

Adding (i) and (ii)

$$\therefore H + H' = (U_2 - U_1) + W + (U_2' - U_1') + W' \quad \dots(iii)$$

$$H + H' = [(U_2 + U_2') - (U_1 + U_1')] + (W + W') \quad \dots(iv)$$

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.

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

$$H = -H'$$

... (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,  $H_1$  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.

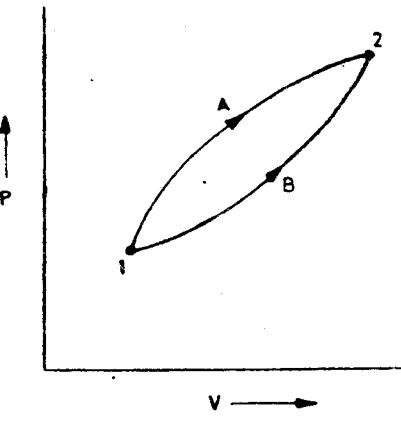


Fig. 6.1

The areas under these curves are different and hence the quantities of work done are also different.

For the path A,

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} P dV \quad \dots(i)$$

For the path B

$$W_B = \int_{1B}^{2B} \delta W = \int_{1B}^{2B} P dV \quad \dots(ii)$$

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*

$$W = \int_{W_1}^{W_2} \delta W = W_2 - W_1 \quad \dots(iii)$$

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

$$\delta H = dU + \delta W \quad \dots(i)$$

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  $\oint \delta H = \oint \delta W \quad \dots(ii)$

[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

$$U_2 - U_1 = 0$$

$$\oint \delta H = \oint \delta W$$

$H = W$  [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

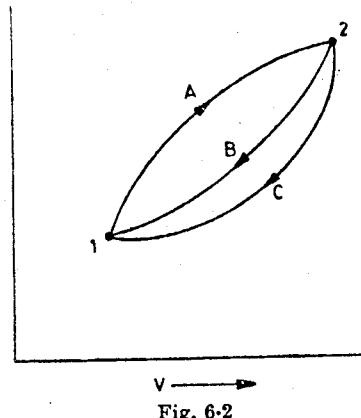


Fig. 6-2

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

$$\int_{1A}^{2A} \delta H + \int_{2B}^{1B} \delta H = \int_{1A}^{2A} \delta W + \int_{2B}^{1B} \delta W \quad \dots(i)$$

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

$$\int_{1A}^{2A} \delta H + \int_{2C}^{1C} \delta H = \int_{1A}^{2A} \delta W + \int_{2C}^{1C} \delta W \quad \dots(ii)$$

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  $\int_{2B}^{1B} (\delta H - \delta W) = \int_{2C}^{1C} (\delta H - \delta W) \quad \dots(iii)$

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.

$$\text{Let } dE = (\delta H - \delta W)$$

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.

$$\therefore \delta H - \delta W = dE \quad \dots(iv)$$

$$\text{or } \delta H = dE + \delta W \quad \dots(v)$$

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.

$E = U + KE + PE + \text{Others}$  which depend upon chemical nature etc.

For a closed system (non-chemical) the changes in all others except  $U$  are insignificant and

$$dE = dU$$

∴ From equation (v)

$$\delta H = dU + \delta W \quad \dots(vi)$$

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  $DB$ .

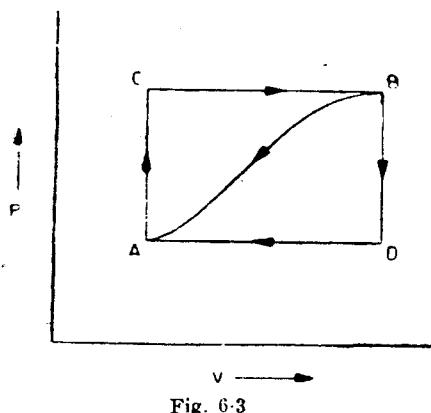


Fig. 6.3

Along the path  $ACB$ ,

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

Here

$$H = +80 \text{ joules}$$

$$W = +30 \text{ joules}$$

∴

$$+80 = U_B - U_A + 30$$

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

(a) Along the path  $ADB$ ,

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

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

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

(b) For the curved path from  $B$  to  $A$ ,

$$W = -20 \text{ joules}$$

$$H = (U_A - U_B) + W$$

$$= -50 - 20 = -70 \text{ joules}$$

(-ve sign shows that heat is liberated by the system)

$$(c) \quad U_A = 0, \quad U_D = 40 \text{ joules}$$

$$U_B - U_A = 50$$

$$\therefore U_B = 50 \text{ joules}$$

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  $DB$

$$H_{DB} = U_C - U_D + W \\ = 50 - 40 + 0 = 10 \text{ joules}$$

## 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,

$$U = f(V, T) \quad \dots(i)$$

Differentiating equation (i)

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

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

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

$$\text{Here } \delta W = P.dV$$

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

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

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

Dividing both sides by  $dT$

$$\frac{\delta H}{dT} = \left( \frac{\partial U}{\partial T} \right)_V + \left( \frac{\partial U}{\partial V} \right)_T \frac{dV}{dT} + \frac{P \cdot dV}{dT}$$

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

If the gas is heated at constant volume,

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

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

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

When the gas is heated at constant pressure,

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

∴ From equation (iv),

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

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

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

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

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

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

$$\therefore C_P - C_V = R$$

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

From equation (iii)

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

For a process at constant temperature

$$dT = 0$$

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

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  $dV$ ,

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

The isobaric volume coefficient of expansion

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

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

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

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

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

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

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

From equations (xii) and (xiv)

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

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

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

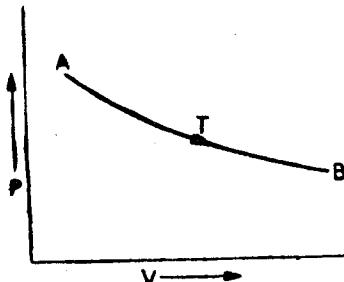


Fig. 6.4

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

$$PV = RT = \text{constant} \quad [\text{For one gram molecule of a gas.}]$$

$$\text{For } n \text{ gram molecules of a gas } PV = nRT$$

#### 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  $0 = dU + \delta W \quad \dots(i)$

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  $\delta W = 0$ .

$$\delta H = dU \quad \dots(ii)$$

The heat transferred in such a process

$$\delta H = C_v \delta T$$

∴  $C_v \delta T = dU \quad \dots(iii)$

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 molecule of working substance,

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

But  $\delta H = C_p dT \quad \dots(ii)$

$$P \cdot dV = r \cdot dT$$

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

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

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

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

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

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

$$\text{But } \delta H = 0$$

$$\text{and } \delta W = P \cdot dV$$

where  $P$  is the pressure of the gas and  $dV$  is the change in volume.

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

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

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

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

For an ideal gas

$$PV = rT$$

Differentiating,

$$P \cdot dV + V \cdot dP = r \cdot dT$$

Substituting the value of  $dT$  in equation (ii),

$$C_v \left[ \frac{P \cdot dV + V \cdot dP}{r} \right] + \frac{P \cdot dV}{J} = 0$$

$$C_v [P \cdot dV + V \cdot dP] + r \cdot \frac{P \cdot dV}{J} = 0$$

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

$$\therefore C_v \cdot P \cdot dV + C_v \cdot V \cdot dP + C_p \cdot P \cdot dV - C_v \cdot P \cdot dV = 0$$

$$C_p \cdot P \cdot dV + C_v \cdot V \cdot dP = 0$$

Dividing by  $C_v \cdot PV$ ,

$$\frac{C_p}{C_v} \cdot \frac{dV}{V} + \frac{dP}{P} = 0$$

$$\text{But } \frac{C_p}{C_v} = \gamma$$

$$\frac{dP}{P} + \gamma \frac{dV}{V} = 0$$

Integrating,  $\log P + \gamma \log V = \text{const.}$

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

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

$$\Rightarrow \log P + \log V^\gamma = \text{const.}$$

or

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

$$\text{Taking } PV = rT$$

$$\text{or } P = \frac{rT}{V}$$

$$\left( \frac{rT}{V} \right) \cdot V^\gamma = \text{const.}$$

But  $r$  is const.

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

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

$$\text{Also } V = \frac{rT}{P}$$

$$P \left[ \frac{rT}{P} \right]^\gamma = \text{const.}$$

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

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

Thus, during an adiabatic process

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

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

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

**Example 6.2.** A motor car tyre has a pressure of 2 atmospheres at the room temperature of  $27^\circ\text{C}$ . If the tyre suddenly bursts, find the resulting temperature.

Here,

$$P_1 = 2 \text{ atmospheres}$$

$$T_1 = 273 + 27$$

$$= 300 \text{ K}$$

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

$$T_2 = ?$$

$$\gamma = 1.4$$

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

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

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

$$0.4 \log (0.5) = 1.4 [\log T_2 - \log 300]$$

$$-0.1204 = 1.4 \log T_2 - 3.4680$$

$$1.4 \log T_2 = 3.4680 - 0.1204$$

$$= 3.3476$$

$$\log T_2 = \frac{3.3476}{1.4}$$

$$= 2.3911$$

$$T_2 = 246.1 \text{ K}$$

$$= -26.9^\circ\text{C}$$

**Example 6.3.** A quantity of air at  $27^\circ\text{C}$  and atmospheric pressure suddenly compressed to half its original volume. Find the (i) pressure and (ii) temperature.

$$(i) P_1 = 1 \text{ atmosphere}; P_2 = ?, \gamma = 1.4$$

$$V_1 = V; \quad V_2 = \frac{V}{2}$$

During sudden compression, the process is adiabatic

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

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

$$= 1[2]^{1.4}$$

$$= 2.636 \text{ atmospheres}$$

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

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

$$\gamma = 1.4$$

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

$$T_2 = T_1 [2]^{1.4-1}$$

$$= 300[2]^{0.4}$$

$$= 395.9 \text{ K}$$

$$= 122.9^\circ\text{C}$$

**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.

$$\begin{aligned} \text{Initial volume} &= V_1 \\ \text{Final volume} &= V_2 \\ &= \frac{V_1}{2} \end{aligned}$$

During an adiabatic process

$$\begin{aligned} T_1 V_1^{\gamma-1} &= T_2 V_2^{\gamma-1} \\ T_2 &= T_1 \left[ \frac{V_1}{V_2} \right]^{\gamma-1} \\ T_2 &= T_1 [2]^{1.40-1} \end{aligned}$$

$$\begin{aligned} \text{But } \gamma \text{ for air} &= 1.40 \\ T_2 &= T_1 [2]^{1.40-1} \\ T_2 &= T_1 [2]^{0.40} \\ T_2 &= 1.319 T_1 \end{aligned}$$

Change in temperature

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

**Example 6.5.** 1 gram molecule of a monoatomic ( $\gamma = 5/3$ ) perfect gas at  $21^\circ\text{C}$  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

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

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

Here,

$$P_2 = 50,$$

$$P_1 = 1,$$

$$T_1 = 273 + 27$$

$$= 300 \text{ K}$$

$$T_2 = ?$$

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

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

$$\begin{aligned} \text{or } \frac{2}{3} \log (50) &= \frac{5}{3} [\log T_2 - \log 300] \\ T_2 &= 1,434 \text{ K} \\ &= 1,161^\circ\text{C} \end{aligned}$$

**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

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

$$T_1 = 300 \text{ K}, \quad T_2 = ?$$

$$\gamma = 1.4$$

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

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

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

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

$$T_2 = 465.5 \text{ K}$$

$$= 192.5^\circ \text{C}$$

The temperature of air increases by

$$192.5 - 27 = 165.5^\circ \text{C} \text{ or } 165.5 \text{ K}$$

**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]

$$(1) \text{ Here, } V_1 = V, \quad V_2 = 3V \\ T_1 = 273 \text{ K} \quad T_2 = ?$$

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

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

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

$$T_2 = 176 \text{ K} = -97^\circ \text{C}$$

$$(2) \text{ Here, } V_1 = V, \quad V_2 = 3V \\ P_1 = 1 \text{ atmosphere,} \quad P_2 = ?$$

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

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

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

$$P_2 = 0.2148 \text{ atmosphere}$$

### 6.16 Slopes of Adiabatics and Isothermals

In an isothermal process

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

Differentiating,

$$PdV + VdP = 0 \Rightarrow \sqrt{dP} = - \frac{P}{V} dV$$

or

$$\frac{dP}{dV} = - \frac{P}{V} \quad \dots(i)$$

In an adiabatic process

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

Differentiating,

$$P\gamma V^{\gamma-2} dV + VdP = 0 \Rightarrow V^{\gamma-1} dP = P\gamma V^{\gamma-1} dV$$

$$\frac{dP}{dV} = - \frac{\gamma P}{V} \quad \dots(ii)$$

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

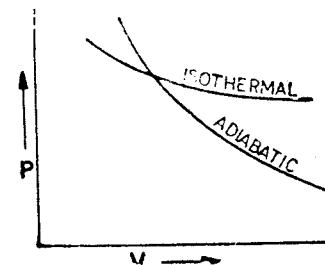


Fig. 6.5

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  $V_2$ ,

$$\text{Work done} = \int_{V_1}^{V_2} P \cdot dV = \text{area } ABba \quad \dots(i)$$

Fig. 6.6 represents the indicator diagram. Considering one gram molecule of the gas

$$PV = RT$$

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

or

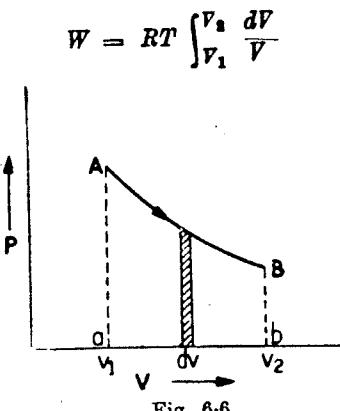


Fig. 6.6

$$= RT \log_e \frac{V_2}{V_1} \quad \dots (ii)$$

$$W = RT \times 2.3026 \log_{10} \frac{V_2}{V_1} \quad \dots (iii)$$

Also

$$P_1 V_1 = P_2 V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$W = RT \times 2.3026 \times \log_{10} \frac{P_1}{P_2} \quad \cancel{\text{W}} \quad \dots (iv)$$

or

∴

Here, the change in the internal energy of the system is zero (because the temperature remains constant). So the heat transferred is equal to the work done.

### 6.18 Work Done During an Adiabatic Process

During an adiabatic process, the gas expands from volume  $V_1$  to  $V_2$ . As shown by the indicator diagram (Fig. 6.7) the work done for an increase in

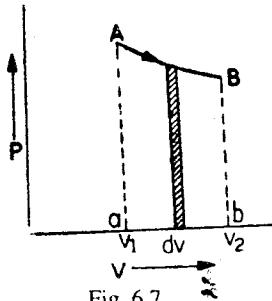


Fig. 6.7.

volume  $dV = P.dV$ . Work done when the gas expands from  $V_1$  to  $V_2$  is given by,

$$W = \int_{V_1}^{V_2} P dV = \text{Area } ABba$$

During an adiabatic process,

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

or

$$P = \frac{K}{V^\gamma}$$

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

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

Since A and B lie on the same adiabatic

$$P_1 V_1^\gamma = P_2 V_2^\gamma = K$$

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

$$W = \frac{1}{1-\gamma} \left[ \frac{P_2 V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1 V_1^\gamma}{V_1^{\gamma-1}} \right]$$

$$= \frac{1}{1-\gamma} [P_2 V_2 - P_1 V_1] \quad \dots (ii)$$

Taking  $T_1$  and  $T_2$  as the temperatures at the points A and B respectively and considering one gram molecule of the gas

$$P_1 V_1 = RT_1$$

$$P_2 V_2 = RT_2$$

Substituting these values in equation (ii)

$$W = \frac{1}{1-\gamma} [RT_2 - RT_1] \quad \dots (iii)$$

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,

$$PdV + VdP = 0 \Rightarrow V dP = P dV$$

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

From the definition of elasticity of a gas

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

$$= \frac{V dP}{-dV} \quad \dots (ii)$$

From (i) and (ii)  
 $E_{iso} = P$

... (iii)

## 2. Adiabatic Elasticity

During an adiabatic process

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

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

or  $\frac{VdP}{dV} = \gamma P$

... (iv)

From the definition of elasticity of a gas

$$\begin{aligned} E_{adi} &= \frac{dP}{-dV/V} \\ &= \frac{V.dP}{-dV} \end{aligned} \quad \dots (v)$$

From (iv) and (v),

$$E_{adi} = \gamma P \quad \dots (vi)$$

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.

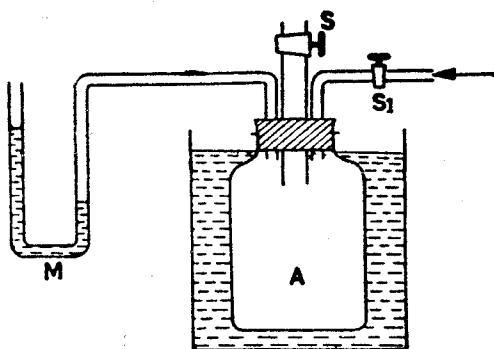


Fig. 6.8

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).

$$P_1 V_1^\gamma = P_0 V_2^\gamma$$

$$\frac{P_1}{P_0} = \left( \frac{V_2}{V_1} \right)^\gamma \quad \dots (i)$$

Finally the point  $C$  is reached. The points  $A$  and  $C$  are at the room temperature. Therefore  $AC$  can be considered as an isothermal.

$$P_1 V_1 = P_2 V_1$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \dots (ii)$$

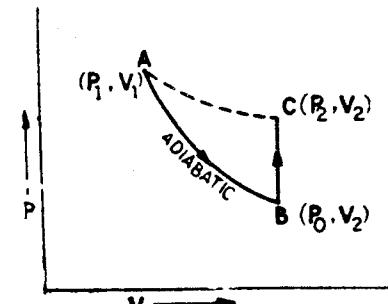


Fig. 6.9

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,

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

$$\gamma = \frac{\log P_1 - \log P_0}{\log P_1 - \log P_2} \quad \dots (iii)$$

Put

$$P_1 = P_0 + H \text{ and } P_2 = P_0 + h$$

∴

$$\gamma = \frac{\log(P_0 + H) - \log P_0}{\log(P_0 + H) - \log(P_0 + h)}$$

$$\gamma = \frac{\log\left(\frac{P_0 + H}{P_0}\right)}{\log\left(\frac{P_0 + H}{P_0 + h}\right)} = \frac{\log\left(1 + \frac{H}{P_0}\right)}{\log\left(1 + \frac{H-h}{P_0+h}\right)}$$

$$\text{Approximately, } \gamma = \frac{\frac{H}{P_0}}{\frac{H-h}{P_0}} = \frac{H}{H-h}$$

$$\text{Hence } \gamma = \frac{H}{H-h} \quad \dots(iv)$$

Similarly,  $\gamma$  for any gas can be determined by this method.

**Drawbacks.** When the stop-cock is opened, a series of oscillations are set up. This is shown by the up and down movement of the liquid in the manometer. Therefore, the exact moment when the stopcock should be closed is not known. The pressure may not be equal to the atmospheric pressure when the stop-cock is closed. It may be higher or less than the atmospheric pressure. Thus the result obtained will not be accurate.

### 6.21 Partington's Method

Lummer, Pringsheim and Partington designed an apparatus to determine the value of  $\gamma$ . In this method, the pressure and temperature are measured accurately before and after the adiabatic expansion.

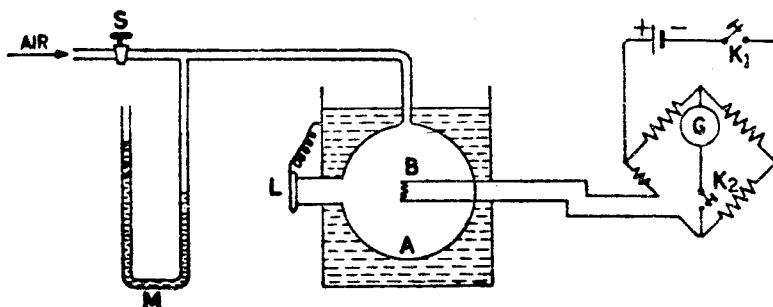


Fig. 6.10

The apparatus consists of a vessel  $A$  having a capacity between 130 and 150 litres. The valve  $L$  can be opened and closed suddenly.

It is controlled by a spring arrangement (Fig. 6.10). Dry air (or gas) at a pressure higher than the atmospheric pressure is forced into the vessel  $A$  and the stop-cock  $S$  is closed. The oil manometer  $M$  is used to measure the pressure of air inside the vessel  $A$ . The bolometer  $B$  (a platinum wire) and a sensitive galvanometer are used in the Wheatstone's bridge arrangement.

The vessel is surrounded by a constant temperature bath. Let the initial pressure and temperature be  $P_1$  and  $T_1$  (room temperature). The bridge is kept slightly disturbed from the balanced position. The valve  $L$  is suddenly opened and closed. The Wheatstones bridge is at once adjusted for balanced position. The temperature of air inside  $A$  has decreased due to adiabatic expansion of air. Let the temperature inside be  $T_0$  and the atmospheric pressure  $P_0$ . If the apparatus is allowed to remain as such for some time, it will gain heat from the surroundings and the balance point gets disturbed. In order that the balance point remains undisturbed, some pieces of ice are added into the water surrounding the vessel  $A$ . When the temperature of water bath is the same as that of air just after adiabatic expansion, the bridge will remain balanced.

The temperature  $T_0$  of the bath represents the temperature of air after the adiabatic expansion.

$$\begin{aligned} \frac{P_1 \gamma^{-1}}{T_1 \gamma} &= \frac{P_0 \gamma^{-1}}{T_0 \gamma} \\ \left(\frac{P_1}{P_0}\right)^{\gamma-1} &= \left(\frac{T_1}{T_0}\right)^{\gamma} \\ (\gamma-1)(\log P_1 - \log P_0) &= \gamma [\log T_1 - \log T_0] \\ \gamma &= \frac{\log P_1 - \log P_0}{(\log P_1 - \log P_0) - (\log T_1 - \log T_0)} \end{aligned}$$

As  $P_1$ ,  $P_0$ ,  $T_1$  and  $T_0$  are known,  $\gamma$  can be calculated. The value of  $\gamma$  for air at 17°C is found to be 1.4034.

**Advantages.** (1) Due to the large volume of the vessel, the expansion is adiabatic.

(2) The temperatures are measured accurately just before and after the adiabatic expansion.

**Drawbacks.** This method cannot be used to find the value of  $\gamma$  at higher temperatures because it is not possible to determine the cooling correction accurately.

### 6.22 Ruchhardt's Experiment

In 1929, Ruchhardt designed an apparatus to find the value of  $\gamma$ . It is based on the principle of mechanics. Air (or gas) is enclosed in a big jar (Fig. 6.11). A tube of uniform area of cross section is fitted and a ball of mass  $m$  fits in the tube just like a piston. In the equilibrium position, the ball is at the point  $A$ . The pressure  $P$  of air inside the vessel, is given by

$$P = P_0 + \frac{mg}{A}$$

### 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 principle of conservation of energy is not violated because the total energy of the system is conserved. It is also clear that, with the initial conditions described above, the three processes will take place.

Let us consider the possibility of the above three processes taking place in the reverse direction. In the first case, if the reverse process is possible, the block *B* should transfer heat to *A* and initial conditions should be restored. In the second case, if the reverse process is possible, the heat energy must again change to kinetic energy and the fly wheel should start rotating with the initial angular velocity  $\omega$ . 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

*Heat and Thermodynamics*

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.

### Q. 25 Second Law of Thermodynamics

A heat engine is chiefly concerned with the conversion of heat energy into mechanical work. A refrigerator is a device to cool a certain space below the temperature of its surroundings. The first law of thermodynamics is a qualitative statement which does not preclude the possibility of the existence of either a heat engine or a refrigerator. The first law does not contradict the existence of a 100% efficient heat engine or a self-acting refrigerator.

In practice, these two are not attainable. These phenomena are recognized and this led to the formulation of a law governing these two devices. It is called second law of thermodynamics.

A new term reservoir is used to explain the second law. A reservoir is a device having infinite thermal capacity and which can absorb, retain or reject unlimited quantity of heat without any change in its temperature.

Kelvin-Planck statement of the second law is as follows :

"It is impossible to get a continuous supply of work from a body (or engine) which can transfer heat with a single heat reservoir. This is a negative statement. According to this statement, a single reservoir at a single temperature cannot continuously transfer heat into work. It means that there should be two reservoirs for any heat engine. One reservoir (called the source) is taken at a higher temperature and the other reservoir (called the sink) is taken at a lower temperature."

According to this statement, zero degree absolute temperature is not attainable because no heat is rejected to the sink at zero degree Kelvin. If an engine works between any temperature higher than zero degree Kelvin and zero degree Kelvin, it means it uses a single reservoir which contradicts Kelvin-Planck's statement of the second law. Similarly, no engine can be 100% efficient.

In a heat engine, the engine draws heat from the source and after doing some external work, it rejects the remaining heat to the sink. The source and sink are of infinite thermal capacity and they maintain constant temperature.

First Part. According to Kelvin, the second law can also be stated as follows :

✓ "It is impossible to get a continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings".

In a heat engine the working substance does some work and rejects the remaining heat to the sink. The temperature of the source must be higher than the surroundings and the engine will not work when the temperatures of the source and the sink are the same. Take the case of a steam engine. The steam (working substance) at high pressure is introduced into the cylinder of the engine. Steam expands, and it does external work. The contents remaining behind after doing work are rejected to the surroundings. The temperature of the working substance rejected to the surroundings is higher than the temperature of the surroundings.

If this working substance rejected by the first engine is used in another engine, it can do work and the temperature of the working substance will fall further.

It means that the working substance can do work only if its temperature is higher than that of the surroundings.

Second Part. According to Clausius :

"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance."

This part is applicable in the case of ice plants and refrigerators. Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature. But, it is possible, if some external work is done on the working substance. Take the case of ammonia ice plant. Ammonia is the working substance. Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted to low pressure vapour. External work is done to compress the ammonia vapours to high pressure. This ammonia at high pressure is passed through coils over which water at room temperature is poured. Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature). This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia. If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

Thus, the second law of thermodynamics plays an important part for practical devices e.g., heat engines and refrigerators. The first law of thermodynamics only gives the relation between the

work done and the heat produced. But the second law of thermodynamics gives the conditions under which heat can be converted into work.

### 6.26 Carnot's Reversible Engine

Heat engines are used to convert heat into mechanical work. Sadi Carnot (French) conceived a theoretical engine which is free from all the defects of practical engines. Its efficiency is maximum and it is an ideal heat engine.

For any engine, there are three essential requisites :

(1) **Source.** The source should be at a fixed high temperature  $T_1$  from which the heat engine can draw heat. It has infinite thermal capacity and any amount of heat can be drawn from it at constant temperature  $T_1$ .

(2) **Sink.** The sink should be at a fixed lower temperature  $T_2$  to which any amount of heat can be rejected. It also has infinite thermal capacity and its temperature remains constant at  $T_2$ .

(3) **Working Substance.** A cylinder with non-conducting sides and conducting bottom contains the perfect gas as the working substance.

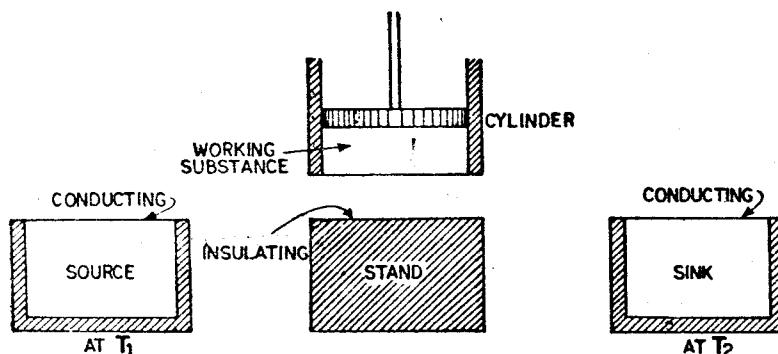


Fig. 6.12.

A perfect non-conducting and frictionless piston is fitted into the cylinder. The working substance undergoes a complete cyclic operation (Fig. 6.12).

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

### Carnot's Cycle

*Q* *2 b* *C* *E* (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)

$$\checkmark W_1 = \int_{V_1}^{V_2} P \cdot dV = RT_1 \log \frac{V_2}{V_1} \\ = \text{area } ABGE \quad \dots(i)$$

(2) Place the engine on the stand having an insulated top. Decrease the pressure on the working substance. The volume

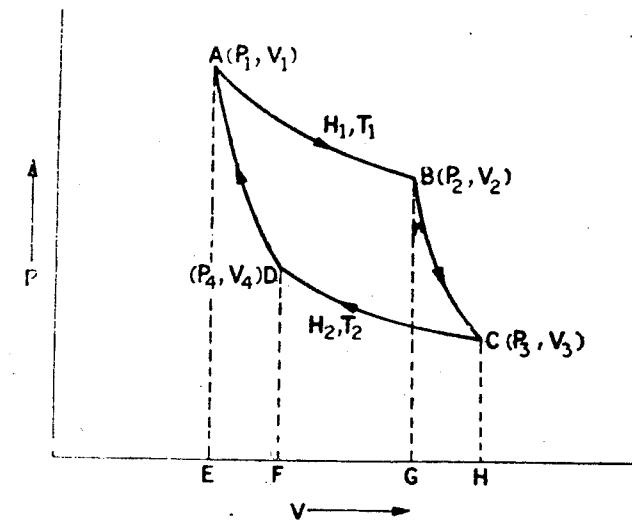


Fig. 6.13

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)

$$\checkmark W_2 = \int_{V_2}^{V_3} P \cdot dV \\ = \int_{V_2}^{V_3} \frac{dV}{V^\gamma} \\ = \frac{V_3 - V_2}{1-\gamma} \quad \Big| \quad \text{But } PV^\gamma = \text{constant} = K \\ P_2 V_2 = R T_1 \\ P_3 V_3 = R T_2 \\ P_3 V_3^\gamma = P_2 V_2^\gamma = K \\ = \frac{P_3 V_3 - P_2 V_2}{1-\gamma} \\ = \frac{R [T_2 - T_1]}{1-\gamma} = \frac{R [T_1 - T_2]}{\gamma-1}$$

$$W_2 = \text{Area } BOHG \quad \dots(ii)$$

(3) Place the engine on the sink at temperature  $T_3$ . 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  $H_3$  is rejected to the sink at temperature  $T_3$ . Finally the point  $D$  is reached.

Work done from  $C$  to  $D$  (isothermal process)

$$\begin{aligned} W_3 &= \int_{V_3}^{V_4} P dV \\ &= RT_2 \log \frac{V_4}{V_3} \\ &= -RT_2 \log \frac{V_3}{V_4} \quad \dots(\text{iii}) \\ W_3 &= \text{area } CHFD \end{aligned}$$

(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).

$$\begin{aligned} W_4 &= \int_{V_4}^{V_1} P dV \\ &= -\frac{R(T_1 - T_2)}{\gamma - 1} \\ W_4 &= \text{Area } DFEA \quad \dots(\text{iv}) \end{aligned}$$

[ $W_3$  and  $W_4$  are equal and opposite and cancel each other.]  $\cancel{1/2 \text{ b end}}$

The net work done by the working substance in one complete cycle

$$\begin{aligned} &= \text{Area } ABGE + \text{Area } BCHG - \text{Area } CHFD \\ &\quad - \text{Area } DFEA \\ &= \text{Area } ABCD \end{aligned}$$

The net amount of heat absorbed by the working substance

$$= H_1 - H_2$$

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

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

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \quad \dots(\text{v})$$

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

$$\begin{aligned} T_1 V_1^{\gamma-1} &= T_2 V_4^{\gamma-1} \\ \frac{T_2}{T_1} &= \left( \frac{V_1}{V_4} \right)^{\gamma-1} \quad \dots(\text{vi}) \end{aligned}$$

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

$$\begin{aligned} T_1 V_2^{\gamma-1} &= T_3 V_3^{\gamma-1} \\ \frac{T_3}{T_1} &= \left( \frac{V_2}{V_3} \right)^{\gamma-1} \quad \dots(\text{vii}) \end{aligned}$$

From (vi) and (vii)

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

From equation (v)

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_1}$$

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

$$W = H_1 - H_2$$

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

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

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

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

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

$$\text{or} \quad \eta = 1 - \frac{H_2}{H_1}$$

$$\eta = 1 - \frac{T_2}{T_1} \quad \dots(\text{viii})$$

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

*Heat and Thermodynamics*

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.

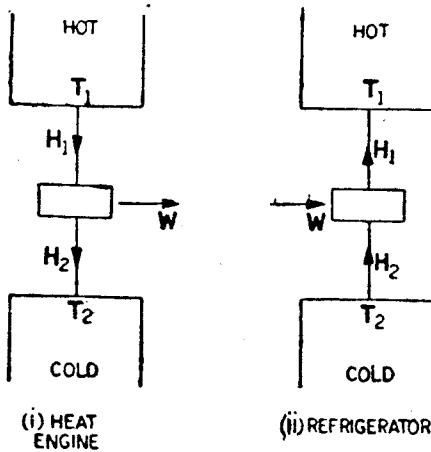


Fig. 6.14

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 performance

$$= \frac{H_2}{W}$$

$$\begin{aligned} &= \frac{H_2}{H_1 - H_2} \\ &= \frac{200}{300 - 200} = 2 \end{aligned}$$

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.

$$T_1 = 273 + 100 = 373 \text{ K}$$

$$T_2 = 273 + 0 = 273 \text{ K}$$

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

$$= 1 - \frac{273}{373} = \frac{100}{373}$$

$$\% \text{ efficiency} = \frac{100}{373} \times 100$$

$$= 26.81\%$$

*Example 6.9.* Find the efficiency of a Carnot's engine working between  $127^\circ\text{C}$  and  $27^\circ\text{C}$ .

$$T_1 = 273 + 127 = 400 \text{ K}$$

$$T_2 = 273 + 27 = 300 \text{ K}$$

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

$$= 1 - \frac{300}{400} = 0.25$$

$$\% \text{ efficiency} = 25\%$$

*Example 6.10.* A Carnot's engine whose temperature of the source is  $400 \text{ K}$  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.

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

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

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

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

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

$$\eta = 1 - \left[ \frac{T_2}{T_1} \right]$$

$$= 1 - \frac{300}{400} = 0.25$$

% 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).

$$T_1 = 450 \text{ K}; \quad T_2 = 350 \text{ K}$$

$$H_1 = 1000 \text{ cal}; \quad H_2 = ?$$

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

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

$$= \frac{1000 \times 350}{450} = 777.77 \text{ cals}$$

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

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

$$= 0.2222$$

% efficiency = 22.22%

Work done in each cycle

$$= H_1 - H_2$$

$$= 1000 - 777.77$$

$$= 222.23 \text{ cal}$$

$$= 222.23 \times 4.2 \text{ joules}$$

$$= 933.33 \text{ joules}$$

**Example 6.12.** A Carnot's engine working as a refrigerator between 260 K and 300 K receives 500 calories of heat from the reservoir at the lower temperature. Calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of work done in each cycle to operate the refrigerator.

[Delhi (Hons.) 1974]

$$H_1 = ? \quad H_2 = 500 \text{ cal}$$

$$T_1 = 300 \text{ K} \quad T_2 = 260 \text{ K}$$

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

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

$$H_1 = \frac{500 \times 300}{260} = 576.92 \text{ cal}$$

$$W = H_1 - H_2 = 76.92 \text{ cal}$$

$$= 76.92 \times 4.2 \text{ joules}$$

$$= 323.08 \text{ joules}$$

**Example 6.13.** A Carnot's refrigerator takes heat from water at 0°C and discards it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the coefficient of performance of the machine?

[Delhi 1974]

$$H_1 = ?$$

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

$$T_1 = 300 \text{ K}$$

$$T_2 = 273 \text{ K}$$

(1)

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

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

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

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

(2) Work done by the refrigerator

$$= W = J(H_1 - H_2)$$

$$W = 4.2(87,900 - 80,000)$$

$$W = 4.2 \times 7900$$

$$W = 3.183 \times 10^4 \text{ joules}$$

or  
(3) Coefficient of performance,

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

$$= \frac{80,000}{87,900 - 80,000}$$

$$= \frac{80,000}{7900}$$

$$= 10.13$$

**Example 6.14.** A Carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased? (Delhi 1971)

In the first case

$$\eta = 50\% = 0.5, \quad T_2 = 273 + 7 = 280 \text{ K.}$$

$$T_1 = ?$$

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

$$\text{or } 0.5 = 1 - \frac{280}{T_1}$$

$$\text{or } T_1 = 560 \text{ K}$$

In the second case

$$\eta' = 70\% = 0.7,$$

$$T_2 = 280 \text{ K,}$$

$$T_1' = ?$$

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

$$0.7 = 1 - \frac{280}{T_1'}$$

$$\text{or } T_1' = 840 \text{ K}$$

$$\text{Increase in temperature} = 840 - 560 = 280 \text{ K}$$

### 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.

*(Carnot's Theorem)* 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  $H_1'$  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*

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

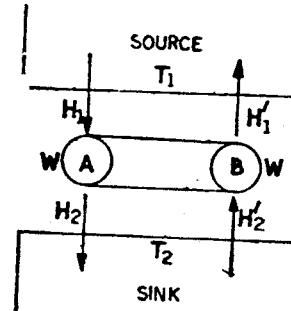


Fig. 6.15.

Efficiency of the engine *B*

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

Since

$$\eta > \eta'; \quad H_1' > H_1$$

Also,

$$W = H_1 - H_2 = H_1' - H_2$$

∴

$$H_2 > H_1$$

Thus, for the two engines *A* and *B* working as a coupled system,  $(H_2 - H_1)$  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  $(H_2 - H_1)$  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.

*End.*

For the same compression ratio, the efficiency of an Otto engine is more than a diesel engine. In practice, the compression ratio for an Otto engine is from 7 to 9 and for a diesel engine it is from 15 to 20. Due to the higher compression ratio, an actual diesel engine has higher efficiency than the Otto (Petrol) engine. The cylinder must be strong enough to withstand very high pressure.

### 6.37 Multicylinder Engines

With an engine having one cylinder, the engine works only during the working stroke. The piston moves during the rest of the three strokes due to the momentum of the shaft. In a multicylinder engine (say 4-cylinder engine) the four cylinders are coupled. The working of each cylinder is given below :—

	<i>First</i>	<i>Second</i>	<i>Third</i>	<i>Fourth</i>
First quarter	Working	Exhaust	Compression	Charging
Second quarter	Exhaust	Charging	Working	Compression
Third quarter	Charging	Compression	Exhaust	Working
Fourth quarter	Compression	Working	Charging	Exhaust

In this way, the power of the engine increases and the shaft gets momentum during each quarter cycle.

### 6.38 Clapeyron Latent Heat Equation

Consider the isothermals  $FBAE$  at temperature  $T+dT$  and  $GCDH$  at temperature  $T$ . Here  $EA$  and  $HD$  show the liquid state

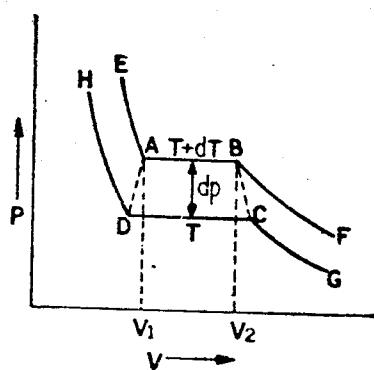


Fig. 6.23

of the substance. At  $A$  and  $D$  the substance is purely in the liquid state (Fig. 6.23). From  $A$  to  $B$  or  $D$  to  $C$  the substance is in transition from the liquid to the gaseous state and vice versa. At  $B$  and  $C$  the substance is purely in the gaseous state. From  $B$  to  $F$  or  $C$  to  $G$  the substance is in the gaseous state. Join  $A$  to  $D$  and  $B$  to  $C$  by dotted lines.

The cycle  $ABCD$  represents a complete cycle and Carnot's theorem can be applied. Suppose the volume at the point  $A$  is  $V_1$ , and temperature is  $T+dT$ . The pressure is just below its saturation pressure and the liquid begins to evaporate and at the point  $B$  the volume is  $V_2$ . The substance is in the vapour state. Suppose the mass of the liquid at  $B$  is one gram. The amount of heat absorbed is  $H_1$ . Here  $H_1 = L + dL$ , where  $L + dL$  is the latent heat of the liquid at temperature  $(T+dT)$ .

At the point  $B$ , the pressure is decreased by  $dP$ . The vapour will expand and its temperature falls. The temperature at  $C$  is  $T$ . At this pressure and temperature  $T$ , the gas begins to condense and is converted into the liquid state. At the point  $D$ , the substance is in the liquid state. From  $C$  to  $D$ , the amount of heat rejected (given out) is  $H_2$ . Here  $H_2 = L$  where  $L$  is the latent heat at temperature  $T$ . By increasing the pressure a little, the original point  $A$  is restored. The cycle  $ABCDA$  is completely reversible. Applying the principle of the Carnot's reversible cycle

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

or

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

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

Here,  $H_1 = L + dL$ ,  $H_2 = L$ ,

$$T_1 = T + dT, T_2 = T$$

$$H_1 - H_2 = L + dL - L = dL$$

$$T_1 - T_2 = T + dT - T = dT$$

$$\therefore \frac{dL}{L} = \frac{dT}{T}$$

The area of the figure

$$\begin{aligned} ABCD &= H_1 - H_2 = dL \\ &= dP(V_2 - V_1) \end{aligned}$$

$$\therefore \frac{dP(V_2 - V_1)}{L} = \frac{dT}{T}$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

... (i)

This is called the Clapeyron's latent heat equation.

**Applications.** (1) *Effect of change of pressure on the melting point.*

When a solid is converted into a liquid, there is change in volume.

(i) If  $V_2$  is greater than  $V_1$ ,

$\frac{dP}{dT}$  is a positive quantity. It means that the rate of change of

pressure with respect to temperature is positive. In such cases, the melting point of the substance will increase with increase in pressure and vice versa.

(ii) If  $V_2$  is less than  $V_1$ .

$\frac{dP}{dT}$  is a negative quantity. It means that the rate of change of pressure with respect to temperature is negative. In such cases, the melting point of the substance will decrease with increase in pressure and vice versa. In the case of melting ice, the volume of water formed is less than the volume of ice taken. Hence  $V_2 < V_1$ .

Therefore, the melting point of ice decreases with increase in pressure. Hence ice will melt at a temperature lower than zero degree centigrade at a pressure higher than the normal pressure.

Ice melts at  $0^\circ\text{C}$  only at a pressure of 76 cm of Hg.

#### (2) Effect of change of pressure on the boiling point.

When a liquid is converted into a gaseous state, the volume  $V_2$  of the gas is always greater than the corresponding volume  $V_1$  of the liquid i.e.  $V_2 > V_1$ .

Therefore,  $\frac{dP}{dT}$  is a +ve quantity.

With increase in pressure, the boiling point of a substance increases and vice versa. The liquid will boil at a lower temperature under reduced pressure. In the case of water, the boiling point increases with increase in pressure and vice versa. Water boils at  $100^\circ\text{C}$  only at 76 cm of Hg pressure. In the laboratories, while preparing steam, the boiling point is less than  $100^\circ\text{C}$  because the atmospheric pressure is less than 76 cm of Hg. In pressure cookers, the liquid boils at a higher temperature because the pressure inside is more than the atmospheric pressure.

**Example 6.17.** Calculate the depression in the melting point of ice produced by one atmosphere increase of pressure. Given latent heat of ice = 80 cal per gram and the specific volumes of 1 gram of ice and water at  $0^\circ\text{C}$  are  $1.091 \text{ cm}^3$  and  $1.000 \text{ cm}^3$  respectively.  
(Panjab 1963)

Here

$$L = 80 \text{ cal} = 80 \times 4.2 \times 10^7 \text{ ergs}$$

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

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

$$= 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$V_1 = 1.091 \text{ cm}^3$$

$$V_2 = 1.000 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \cdot T \cdot (V_2 - V_1)}{L}$$

$$= \frac{76 \times 13.6 \times 980 \times 273(1 - 1.091)}{80 \times 4.2 \times 10^7}$$

$$= -0.0074 \text{ K}$$

Therefore, the decrease in the melting point of ice with an increase in pressure of one atmosphere

$$= 0.0074 \text{ K} = 0.0074^\circ\text{C}$$

**Example 6.18.** Find the increase in the boiling point of water at  $100^\circ\text{C}$  when the pressure is increased by one atmosphere. Latent heat of vaporisation of steam is 540 cal/gram and 1 gram of steam occupies a volume of  $1677 \text{ cm}^3$ .

$$dP = 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$T = 100 + 273$$

$$= 373 \text{ K}$$

$$L = 540 \times 4.2 \times 10^7 \text{ ergs}$$

$$V_1 = 1.000 \text{ cm}^3$$

$$V_2 = 1677 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \times T(V_2 - V_1)}{L}$$

$$= \frac{76 \times 13.6 \times 980 \times 373 \times 1676}{540 \times 4.2 \times 10^7}$$

$$= 27.92^\circ\text{C}$$

Therefore, the increase in the boiling point of water with an increase in pressure of one atmosphere

$$= 27.92^\circ\text{C}$$

$$= 27.92 \text{ K}$$

**Example 6.19.** Calculate the change in temperature of boiling water when the pressure is increased by 27.12 mm of Hg. The normal boiling point of water at atmospheric pressure is  $100^\circ\text{C}$ .

$$\text{Latent heat of steam} = 537 \text{ cal/g}$$

and specific volume of steam =  $1674 \text{ cm}^3$  (Delhi 1974)

$$dP = 2.712 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$T = 100 + 273 = 373 \text{ K}$$

$$L = 537 \times 4.2 \times 10^7 \text{ ergs}$$

$$V_1 = 1.000 \text{ cm}^3$$

$$V_2 = 1674 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$= 2.792 \text{ K}$$

$$= 2.792^\circ\text{C}$$

Therefore, the increase in the boiling point of water with an increase of 0.1 atmosphere pressure

$$= 2.792 \text{ K}$$

$$= 2.792^\circ\text{C}$$

**Example 6.23.** Calculate the change in the melting point of ice when it is subjected to a pressure of 100 atmospheres.

Density of ice =  $0.917 \text{ g/cm}^3$  and

Latent heat of ice =  $336 \text{ J/g}$

(Delhi 1972)

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 100 - 1$$

$$= 99 \text{ atmospheres}$$

$$dP = 99 \times 76 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$L = 336 \text{ J/g}$$

$$= 336 \times 10^7 \text{ ergs/g}$$

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

$$(V_2 - V_1) = 1 - \frac{1}{0.917}$$

$$= -\frac{0.083}{0.917}$$

$$= -0.091 \text{ cm}^3$$

$$dT = \frac{T dP (V_2 - V_1)}{L}$$

$$dT = \frac{273 \times 99 \times 76 \times 13.6 \times 980 \times (-0.091)}{336 \times 10^7}$$

$$dT = -0.7326 \text{ K}$$

$$= -0.7326^\circ\text{C}$$

The decrease in the melting point of ice with a pressure of 100 atmospheres

$$= 0.7326^\circ\text{C}$$

**Example 6.24** Calculate the pressure required to lower melting point of ice by  $1^\circ\text{C}$ .

( $L = 79.6 \text{ cal/g}$ , specific volume of water at  $0^\circ\text{C} = 1.000 \text{ cm}^3$ , specific volume of ice at  $0^\circ\text{C} = 1.091 \text{ cm}^3$  and 1 atmosphere pressure =  $1.013 \times 10^6 \text{ dynes/cm}^2$ ). (Delhi 1973)

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = -1 \text{ K}$$

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

$$V_2 - V_1 = -0.091 \text{ cm}^3$$

$$L = 79.6 \text{ cal/g}$$

$$= 79.6 \times 4.18 \times 10^7 \text{ ergs/g}$$

$$dP = \frac{L \cdot dT}{T(V_2 - V_1)}$$

$$dP = \frac{79.6 \times 4.18 \times 10^7 \times 1}{273 \times 0.091} \text{ dynes/cm}^2$$

$$dP = \frac{79.6 \times 4.18 \times 10^7}{273 \times 0.091 \times 1.013 \times 10^6} \text{ atmospheres}$$

$$dP = 135.2 \text{ atmospheres}$$

∴ Pressure required

$$= 135.2 + 1$$

$$= 136.2 \text{ atmospheres}$$

**Example 6.25.** Water boils at a temperature of  $101^\circ\text{C}$  at a pressure of 787 mm of Hg. 1 gram of water occupies  $1.601 \text{ cm}^3$  on evaporation. Calculate the latent heat of steam.  $J = 4.2 \times 10^7 \text{ ergs/cal}$ . (Delhi (Hons.) 1971)

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dP = 787 - 760$$

$$= 27 \text{ mm of Hg}$$

$$= 2.7 \text{ cm of Hg}$$

$$= 2.7 \times 13.6 \times 980 \text{ dynes/cm}^2$$

$$dT = 1^\circ\text{C} = 1\text{K}$$

$$T = 373 \text{ K}$$

$$V_2 - V_1 = 1.601 - 1 = 1.600 \text{ cm}^3$$

$$L = ?$$

$$L = \frac{T dP (V_2 - V_1)}{dT}$$

$$L = \frac{373 \times 2.7 \times 13.6 \times 980 \times 1.600}{1} \text{ ergs/g}$$

$$L = \frac{373 \times 2.7 \times 13.6 \times 980 \times 1.600}{4.2 \times 10^7} \text{ cal/g}$$

$$L = 511.3 \text{ cal/g}$$

**Example 6.26.** When lead is melted at atmospheric pressure, (the melting point is  $600 \text{ K}$ ) the density decreases from  $11.01$  to  $10.65 \text{ g/cm}^3$  and the latent heat of fusion is  $24.5 \text{ J/g}$ . What is the melting point at a pressure of 100 atmospheres? (Delhi (Hons.) 1972)

Here

$$H_1 = +1000 \text{ joules}$$

$$H_2 = -800 \text{ joules} \text{ (since heat is rejected)}$$

$$T_1 = 500 \text{ K}$$

$$T_2 = 300 \text{ K}$$

$$\sum \frac{H}{T} = \frac{1000}{500} + \frac{-800}{300}$$

$$= -\frac{2}{3} \text{ joule/degree}$$

(3) Consider a Carnot's reversible engine working between the temperatures 500 K and 300 K. Suppose 1000 joules of heat energy is drawn from the high temperature reservoir.

Here

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

$$\frac{1000}{500} = \frac{H_2}{300}$$

or

$$H_2 = 600 \text{ joules}$$

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

Here

$$H_1 = +1000 \text{ joules}$$

$$H_2 = -600 \text{ joules}$$

$$T_1 = 500 \text{ K}$$

$$T_2 = 300 \text{ K}$$

∴

$$\sum \frac{H}{T} = \frac{1000}{500} + \frac{(-600)}{300}$$

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

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

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

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

$$\int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} = 0 \quad \dots(ii)$$

From equations (i) and (ii)

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

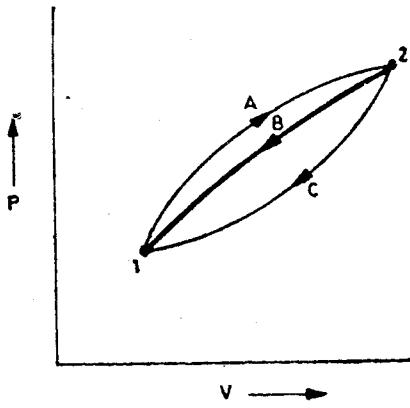


Fig. 6.25

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

$$dS = \frac{\delta H}{T} \quad \dots(iv)$$

$$\text{or} \quad S_2 - S_1 = \int_1^2 \frac{\delta H}{T} \quad \dots(v)$$

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

$$\oint \delta H = 0$$

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

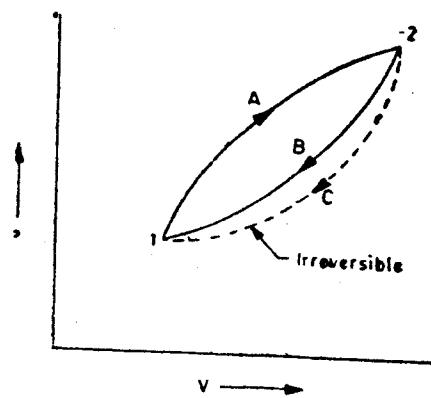


Fig. 6-26

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

Applying Clausius inequality for the cycle of processes *A* and *O*

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

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

From equations (i) and (ii)

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

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

$$\begin{aligned} \int_{2B}^{1B} \frac{\delta H}{T} &= \int_{2B}^{1B} dS = \int_{2O}^{1O} dS \\ \therefore dS &> \frac{\delta H}{T} \quad \dots(iii) \\ S_2 - S_1 &> \int_1^2 \delta H \quad \dots(iv) \end{aligned}$$

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

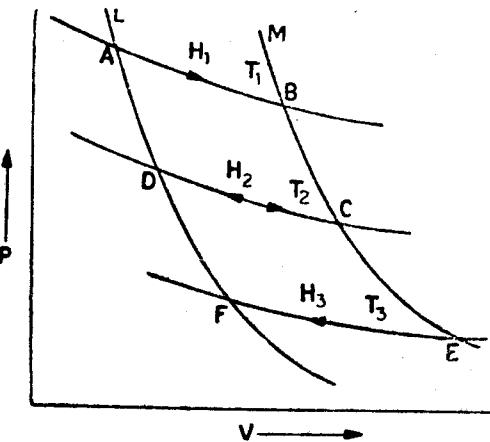


Fig. 6-27

there is change in volume and temperature. This shows that all along the adiabatics *L* or *M*, there is change of temperature. Consider the isotherms at temperatures *T*<sub>1</sub>, *T*<sub>2</sub> and *T*<sub>3</sub>. *ABCD* represents the Carnot's reversible cycle. From *A* to *B*, heat energy *H*<sub>1</sub> is absorbed at temperature *T*<sub>1</sub>. From *C* to *D*, heat energy *H*<sub>2</sub> is rejected at temperature *T*<sub>2</sub>.

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

Similarly considering the cycle *DCEF*

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

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

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*<sub>1</sub> and *S*<sub>2</sub> respectively.

Here *S*<sub>1</sub> and *S*<sub>2</sub> 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

$$dS = \frac{\delta H}{T} \quad \dots(1)$$

In general, the change in entropy

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

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

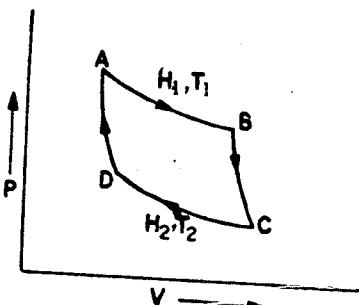


Fig. 6.28

ing substance at temperature  $T_1$ . The gain in entropy of the working substance from  $A$  to  $B$  is  $H_1/T_1$ . ( $H_1/T_1$  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  $D$  is  $H_2/T_2$ . ( $H_2/T_2$  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

the total gain in entropy by the working substance in the cycle  $ABCDA$

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

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.

$$\text{Loss in entropy of the hot body} = \frac{H}{T_1}$$

$$\text{Gain in entropy of the cold body} = \frac{H}{T_2}$$

Therefore, the total increase in entropy of the system

$$= \frac{H}{T_2} - \frac{H}{T_1}$$

It is a positive quantity because  $T_2$  is less than  $T_1$ . Thus the entropy of the system increases in all irreversible processes.

#### 6.47 Third Law of Thermodynamics

In all heat engines, there is always loss of heat in the form of conduction, radiation and friction. Therefore, in actual heat engines

$\frac{H_1}{T_1}$  is not equal to  $\frac{H_2}{T_2}$  ..

$\therefore \frac{H_1}{T_1} - \frac{H_2}{T_2}$  is not zero but it is a positive quantity. When

cycle after cycle is repeated, the entropy of the system increases and tends to a maximum value. When the system has attained the maximum value, a stage of stagnancy is reached and no work can be done by the engine at this stage. In this universe the entropy is increasing and ultimately the universe will also reach a maximum value of entropy when no work will be possible. With the increase in entropy, the disorder of the molecules of a substance increases. The entropy is also a measure of the disorder of the system. With

decrease in entropy, the disorder decreases. At absolute zero temperature, the entropy tends to zero and the molecules of a substance or a system are in perfect order (well arranged). 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 state. 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

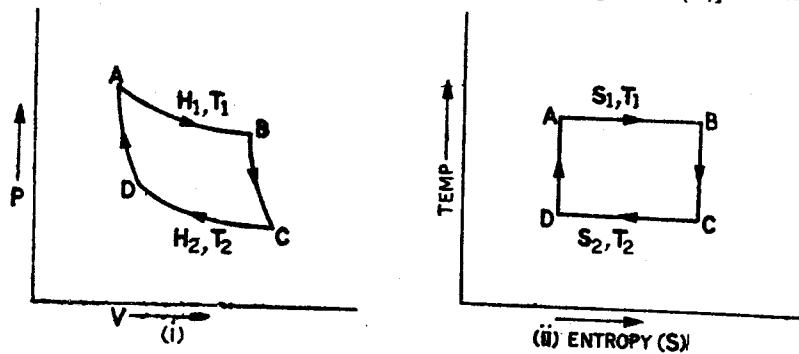


Fig. 6.29

B to C, there is no change in entropy. The temperature 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)].

$$\text{The area } ABCD = S_1(T_1 - T_2) = S_2(T_2 - T_1)$$

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

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

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

Therefore, the area ABCD represents the energy converted to work

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

Here  $H_2$  is the unavailable energy.

$$H_2 = \frac{H_1}{T_1} \times T_2 = S_1 \times T_2$$

The unavailable energy depends on the change in entropy at temperature  $T_1$  and the temperature  $T_2$ .

#### 6.49 Entropy of Perfect Gas

Consider one gram of a perfect gas at a pressure  $P$ , volume  $V$  and temperature  $T$ . Let the quantity of heat given to the gas be  $\delta H$ .

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

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

$$\delta H = TdS$$

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

$$\text{Also } PV = rT$$

$$P = \frac{rT}{V}$$

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

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

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

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

$$S_2 - S_1 = C_V \times 2.3026 \log_{10} \frac{T_2}{T_1} + \frac{r}{J} \times 2.3026 \log_{10} \frac{V_2}{V_1} \quad \dots(iv)$$

The change in entropy can be calculated in terms of pressure also.

$$PV = rT$$

Differentiating

$$PdV + VdP = rdT$$

$$PdV = rdT - VdP$$

Substituting the value of  $PdV$  in equation (ii)

$$TdS = C_V \times dT + \frac{rdT}{J} - \frac{VdP}{J}$$

$$TdS = \left( C_V + \frac{r}{J} \right) dT - \frac{VdP}{J}$$

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

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

Also  $PV = rT$

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

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

Integrating

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

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

$$S_2 - S_1 = C_P \times 2.3026 \times \log_{10} \frac{T_2}{T_1} - \frac{r}{J} \times 2.3026 \log_{10} \frac{P_2}{P_1} \quad \dots(vi)$$

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

$$S_2 - S_1 = C_P \times 2.3026 \log_{10} \frac{T_2}{T_1} - \frac{R}{J} \times 2.3026 \log_{10} \frac{P_2}{P_1} \quad \dots(vii)$$

**Example 6.29.** Calculate the change in entropy when 10 grams of ice at  $0^\circ\text{C}$  is converted into water at the same temperature.

(Punjab 1963, Delhi 1975)

Heat absorbed by 10 g of ice at  $0^\circ\text{C}$  when it is converted into water at  $0^\circ\text{C} = 10 \times 80 = 800 \text{ cal}$

$$\therefore \delta H = 800 \text{ cal}$$

$$T = 0^\circ\text{C} = 273 \text{ K}$$

The gain in entropy

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

$$= \frac{800}{273} = 2.93 \text{ cal/K}$$

**Example 6.30.** Calculate the change in entropy when 5 kg of water at  $100^\circ\text{C}$  is converted into steam at the same temperature.

Heat absorbed by 5 kg of water at  $100^\circ\text{C}$  when it is converted into steam at  $100^\circ\text{C}$

$$= 5000 \times 540$$

$$= 2700000 \text{ cal}$$

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

The gain in entropy

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

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

**Example 6.31.** Calculate the increase in entropy when 1 gram of ice at  $-10^\circ\text{C}$  is converted into steam at  $100^\circ\text{C}$ . 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  $-10^\circ\text{C}$  to  $0^\circ\text{C}$

$$\begin{aligned} dS &= \int_{T_1}^{T_2} \frac{\delta H}{T} \\ &= ms \int_{T_1}^{T_2} \frac{dT}{T} \\ &= ms \log_e \frac{T_2}{T_1} \\ &= ms \times 2.3026 \log_{10} \frac{T_2}{T_1} \\ &= 1 \times 0.5 \times 2.3026 \log_{10} \frac{273}{263} \\ &= 0.01865 \text{ cal/K} \end{aligned}$$

(2) Increase in entropy when 1 gram of ice at  $0^\circ\text{C}$  is converted into water at  $0^\circ\text{C}$ .

$$\begin{aligned} dS &= \frac{\delta H}{T} \\ &= \frac{80}{273} = 0.293 \text{ cal/K} \end{aligned}$$

(3) Increase in entropy when the temperature of 1 g of water is raised from  $0^\circ\text{C}$  to  $100^\circ\text{C}$ .

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

$$= m_1 \times 2.3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 1 \times 2.3026 \log_{10} \frac{373}{273}$$

$$= 0.312 \text{ cal/K}$$

(4) Increase in entropy when 1 g water at 100°C is converted into steam at 100°C

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

$$= \frac{540}{373} = 1.447 \text{ cal/K}$$

Total increase in entropy

$$= 0.01865 + 0.293 + 0.312 + 1.447$$

$$= 2.07065 \text{ cal/K}$$

*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.

$$\text{Work done} = \int_{V_1}^{V_2} P dV$$

$$\text{But } PV = RT$$

or

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

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

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

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

$$W = RT \times 2.3026 \log_{10} 4 \quad (4)$$

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

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

$$= \frac{W}{JT} = \frac{RT \times 2.3026 \log_{10} 4}{JT}$$

$$= 1.387 \frac{R}{J} \text{ cal/K}$$

*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)

$$(i) m_1 = 50 \text{ g}; T_1 = 273 \text{ K}$$

$$m_2 = 50 \text{ g}; T_2 = 353 \text{ K}$$

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.

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

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

$$= 50 \times 1 \times \log_e \frac{313}{273}$$

$$= 50 \times 2.3026 \times \log_{10} \frac{313}{273}$$

$$= +6.829 \text{ cal/K}$$

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

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

$$= 50 \times 1 \times \log_e \frac{313}{353}$$

$$= 50 \times 2.3026 \times \log_{10} \frac{313}{353}$$

$$= -6.023 \text{ cal/K}$$

Here, the -ve sign indicates loss in entropy.

Therefore, the total gain in entropy of the system

$$= 6.829 - 6.023$$

$$= 0.806 \text{ cal/K}$$

*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)

$$m_1 = 50 \text{ g}$$

$$T_1 = 15 + 273 = 288 \text{ K}$$

$$m_2 = 80 \text{ g}$$

$$T_2 = 40 + 273 = 313 \text{ K}$$

Let the final temperature be  $T$  K.

$$m_1 \times s \times (T - T_1) = m_2 \times s \times (T_2 - T)$$

$$50 \times 1 \times (T - 288) = 80 \times 1 \times (313 - T)$$

$$T = 303.4 \text{ K}$$

(ii) Change in entropy when the temperature of 50 g of water rises from 288 K to 303.4 K

$$\begin{aligned} \frac{\delta H}{T} &= ms \int_{T_1}^T \frac{dT}{T} \\ &= 50 \times 1 \times 2.3026 \times \log_{10} \frac{303.4}{288} \\ &= +2.602 \text{ cal/K.} \end{aligned}$$

(iii) Change in entropy when the temperature of 80 g of water decreases from 313 K to 303.4 K

$$\begin{aligned} \frac{\delta H}{T} &= ms \int_{T_2}^T \frac{dT}{T} \\ &= 80 \times 1 \times 2.3026 \times \log_{10} \frac{303.4}{313} \\ &= -2.487 \text{ cal/K.} \end{aligned}$$

Therefore, the net change in the entropy of the system

$$\begin{aligned} &= +2.602 - 2.487 \\ &= +0.115 \text{ cal/K.} \end{aligned}$$

Hence the net increase in the entropy of the system

$$= 0.115 \text{ cal/K.}$$

**Example 6.35.** 10 g of steam at 100°C is blown into 90 grams of water at 0°C, contained in a calorimeter of water equivalent 10 grams. The whole of the steam is condensed. Calculate the increase in the entropy of the system.  
[Delhi (Hons.) 1973]

(i)

$$m_1 = 10 \text{ g}$$

$$T_1 = 100^\circ\text{C} = 373 \text{ K}$$

$$m_2 = 90 + 10 = 100 \text{ g}$$

$$T_2 = 273 \text{ K}$$

Let the final temperature be  $T$  K

$$10 \times 540 + 10(373 - T) = 100(T - 273)$$

$$T = 331.2 \text{ K}$$

(ii) Change in entropy when the temperature of water and calorimeter rises from 273 K to 331.2 K

$$\begin{aligned} \frac{\delta H}{T} &= ms \int_{T_1}^T \frac{dT}{T} \\ &= 100 \int_{273}^{331.2} \frac{dT}{T} \end{aligned}$$

$$\begin{aligned} &= 100 \times 2.3026 \times \log_{10} \left( \frac{331.2}{273} \right) \\ &= +19.32 \text{ cal/K.} \end{aligned}$$

(iii) Change in entropy when 10 grams of steam at 373 K is condensed to water at 373 K

$$\begin{aligned} \frac{\delta H}{T} &= - \frac{10 \times 540}{273} \\ &= -14.47 \text{ cal/K.} \end{aligned}$$

(—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

$$\begin{aligned} \frac{\delta H}{T} &= ms \int_{T_2}^T \frac{dT}{T} \\ &= 10 \times 2.3026 \log_{10} \left( \frac{331.2}{373} \right) \\ &= -1.188 \text{ cal/K.} \end{aligned}$$

Net change in entropy

$$\begin{aligned} &= 19.32 - 14.47 - 1.188 \\ &= +3.662 \text{ cal/K.} \end{aligned}$$

Hence the net increase in the entropy of the system

$$= 3.662 \text{ cal/K.}$$

**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.

$$\begin{aligned} dS &= \frac{\delta H}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T} \\ &= 1 \times 4.2 \int_{293}^{273} \frac{dT}{T} \\ &= 4.2 \times 2.3026 \log_{10} \left( \frac{273}{293} \right) \\ &= -0.2969 \text{ J/K.} \end{aligned}$$

(ii) Change in entropy when 1 g of water at 273 K is converted into ice at 273 K

$$dS = \frac{\delta H}{T} = \frac{-1 \times 335}{273} = -1.227 \text{ J/K}$$

(iii) Change in entropy when the temperature of 1 g of ice at 273 K falls to 263 K

$$\begin{aligned} dS &= \frac{\delta H}{T} = ms \int_{T_1}^{T_2} \frac{dT}{T} \\ &= 1 \times 2.1 \times 2.3026 \log_{10} \left( \frac{263}{273} \right) \\ &= -0.07834 \text{ J/K} \end{aligned}$$

Total change in entropy of the system

$$\begin{aligned} &= -0.2969 - 1.227 - 0.07834 \\ &= -1.60224 \text{ J/K} \end{aligned}$$

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 (i) 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

$$\begin{aligned} dS &= \int_{T_1}^{T_2} \frac{\delta H}{T} \\ &= ms \times 2.3026 \log_{10} \frac{T_2}{T_1} \\ &= 1000 \times 1 \times 2.3026 \log_{10} \frac{373}{273} \\ &= 312 \text{ cal/K} \end{aligned}$$

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

$$\begin{aligned} dS &= \frac{-\delta H}{T} \\ &= -\frac{1000 \times 1 \times 100}{373} = -268.1 \text{ cal/K} \end{aligned}$$

Negative sign shows decrease in entropy

(2) (ii) Change in entropy of the universe

$$\begin{aligned} &= 312 - 268.1 \\ &= 43.9 \text{ cal/K} \end{aligned}$$

Therefore, the net increase in entropy of the universe

$$= 43.9 \text{ cal/K}$$

### 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

$$\delta H = dU + dW$$

$$\delta H = dU + PdV$$

$$\delta U = \delta H - PdV$$

or

From the second law of thermodynamics,

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

or

$$\delta S = TdS$$

Substituting this value of  $\delta H$  in the first equation

$$dU = TdS - PdV \quad \dots(i)$$

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)

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

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

Comparing the coefficients of  $dx$  and  $dy$ , we get

$$\left( \frac{\partial U}{\partial x} \right)_y = T \left( \frac{\partial S}{\partial x} \right)_y - P \left( \frac{\partial V}{\partial x} \right)_y \quad \dots(ii)$$

$$\left( \frac{\partial U}{\partial y} \right)_x = T \left( \frac{\partial S}{\partial y} \right)_x - P \left( \frac{\partial V}{\partial y} \right)_x \quad \dots(iii)$$

Differentiating equation (ii) with respect to  $y$  and equation (iii) with respect to  $x$

$$\begin{aligned} \frac{\partial^2 U}{\partial y \partial x} &= \left( \frac{\partial T}{\partial y} \right)_z \left( \frac{\partial S}{\partial x} \right)_y + T \frac{\partial^2 S}{\partial y \partial x} \\ &\quad - \left( \frac{\partial P}{\partial y} \right)_x \left( \frac{\partial V}{\partial x} \right)_y - P \frac{\partial^2 V}{\partial y \partial x} \end{aligned}$$

and

$$\begin{aligned} \frac{\partial^2 U}{\partial x \partial y} &= \left( \frac{\partial T}{\partial x} \right)_y \left( \frac{\partial S}{\partial y} \right)_x + T \frac{\partial^2 S}{\partial x \partial y} \\ &\quad - \left( \frac{\partial P}{\partial x} \right)_y \left( \frac{\partial V}{\partial y} \right)_x - P \frac{\partial^2 V}{\partial x \partial y} \end{aligned}$$

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

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

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

Simplifying,

$$\begin{aligned} \left( \frac{\partial T}{\partial y} \right)_z \left( \frac{\partial S}{\partial x} \right)_y - \left( \frac{\partial P}{\partial y} \right)_x \left( \frac{\partial V}{\partial x} \right)_y \\ = \left( \frac{\partial T}{\partial x} \right)_y \left( \frac{\partial S}{\partial y} \right)_x - \left( \frac{\partial P}{\partial x} \right)_y \left( \frac{\partial V}{\partial y} \right)_x \quad \dots(iv) \end{aligned}$$

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

$$x = T$$

$$y = V$$

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

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

Substituting these values in equation (iv)

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

But

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

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

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

$$x = T$$

$$y = P$$

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

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

78. Derive the following relations :

$$(a) C_p - C_v = -T \left( \frac{\partial V}{\partial T} \right)_P^2 \left( \frac{\partial P}{\partial V} \right)_T$$

$$(b) TdS = C_P dT - T \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$(c) \frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{\gamma}{\gamma - 1}.$$

[Delhi (Hons.), 1978]

✓ 79. Write short notes on :

- (i) Isothermal Process
- (ii) Adiabatic Process
- (iii) Isochoric Process
- (iv) Carnot's engine
- (v) Carnot's theorem
- (vi) Second Law of thermodynamics
- (vii) Clement and Desormes' method
- (viii) Ruchhardt's experiment for  $\gamma$
- (ix) Absolute gas scale
- (x) Rankine cycle
- (xi) Diesel engine
- (xii) Steam engine
- (xiii) Otto cycle
- (xiv) Entropy is a measure of disorder
- (xv) Entropy tends to a maximum
- (xvi) Third Law of thermodynamics
- (xvii) Absolute zero temperature

[Delhi, 1975]

- (xviii) Entropy of a perfect gas
- (xix) Temperature-Entropy diagram
- (xx) Thermodynamic system
- (xxi) Thermal Equilibrium
- (xxii) Concept of Temperature
- (xxiii) Concept of Heat
- (xxiv) Zeroth Law in Thermodynamics.

[Delhi (Hons.) 1977]

(xxv) Phase changes of the second order. [Delhi (Hons.) 75]

80. A motor car tyre has a pressure of 3 atmospheres at the room temperature of 27°C. If the tyre suddenly bursts what is the resulting temperature ? [Ans. 218.6 K = -54.4°C]

81. A quantity of air ( $\gamma = 1.4$ ) at 27°C is compressed suddenly to  $\frac{1}{4}$  of its original volume. Find the final temperature. [Ans. 522.3 K = 249.3°C]

82. A quantity of air at 27°C and atmospheric pressure is suddenly compressed to  $\frac{1}{4}$  of its original volume. Find (i) the final pressure and (ii) the final temperature.

[Ans. (i) 8.29 atmospheres (ii) 571.1 K = 298.1°C]

83. Find the efficiency of the Carnot's engine working between 150°C and 50°C. [Ans. 23.64%]

84. Find the efficiency of a Carnot's engine working between 227°C and 27°C. [Ans. 40%]

85. A Carnot's engine whose temperature of the source is 400 K takes 500 calories of heat at this temperature and rejects 400 calories of heat to the sink. What is the temperature of the sink ? Calculate the efficiency of the engine.

[Ans. (i) 320 K, (ii) 20%]

86. A Carnot's engine is operated between two reservoirs at temperatures of 500 K and 400 K. If the engine receives 2000 calories of heat from the source in each cycle, calculate (a) the amount of heat rejected to the sink in each cycle, (b) the efficiency of the engine and (c) the work done by the engine in each cycle in (i) joules (ii) kilo-Watt hours.

[Ans. (a) 1600 calories, (b) 20%, (c) (i) 1780 joules, (ii)  $4.944 \times 10^{-4}$  kWh]

87. A Carnot's engine working as a refrigerator between 250 K and 300 K receives 1000 calories of heat from the reservoir at the lower temperature. (i) Calculate the amount of heat rejected to the reservoir at the higher temperature. (ii) Calculate also the amount of work done in each cycle to operate the refrigerator.

[Ans. (i) 1200 cal, (ii) 840 joules]

88. Calculate the depression in the melting point of ice produced by 2 atmospheres increase of pressure. Given latent heat of ice = 80 cal/g and the specific volumes of 1 gram of ice and water at 0°C are  $1.091 \text{ cm}^3$  and  $1.000 \text{ cm}^3$  respectively.

[Ans. 0.0148 K or 0.0148°C]

89. Find the increase in the boiling point of water at 100°C when the pressure is increased by 2 atmospheres. Latent heat of vaporisation of steam is 540 cal/g and 1 g of steam occupies 1677  $\text{cm}^3$  volume.

[Ans. 55.84 K or 55.84°C]

90. Calculate the change in the melting point of naphthalene for 2 atmospheres rise in pressure, given that its melting point is 80°C. Latent heat of fusion is 4563 cal/mol and increase in volume on fusion is  $18.7 \text{ cm}^3/\text{mol}$ . 1 cal =  $4.2 \times 10^7$  ergs.

[Ans. -0.06976 K or -0.06976°C]

91. Calculate the temperature at which ice will freeze if the pressure is increased by 135.2 atmospheres. The change in specific volume when 1 gram of water freezes into ice is  $0.091 \text{ cm}^3$ . One atmospheric pressure =  $10^6$  dynes/cm $^2$ . Latent heat of fusion of ice = 80 cal/g, and  $J = 4.2 \times 10^7$  ergs/cal.

[Ans. -1.0°C]

92. Calculate the temperature at which water will boil if the pressure is increased by 1.814 atmospheres. Given that the change in specific volume when one gram of water is converted into steam is  $1676 \text{ cm}^3$ . Latent heat of vaporization of steam = 540 cal/g.  $J = 4.2 \times 10^7$  ergs/cal and one atmosphere pressure =  $10^6$  dynes/cm $^2$ .

[Ans. 150°C]

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