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SYLLABUS

B.Sc. II Physics

PAPER – I : HEAT AND THERMODYNAMICS

SC-116

CHAPTER-1 : KINETIC THEORY OF MATTER

Ideal Gas : Kinetic model, deduction of Boyle's law, interpretation of temperature, estimation of rms speeds of molecules, Brownian motion, estimate of the Avagadro number. Equipartition of energy, specific heat of monoatomic gas, extension to di- and triatomic gases. Behaviour at low temperatures. Adiabatic expansion of an ideal gas.

Real Gas : Vander Waal gas, equation of state, nature of Vander Waals forces, comparison with experimental P-V curves. Jule expansion of ideal gas, and of a Vander Waals gas, Joule coefficient, estimates of J-T cooling.

CHAPTER-2 : LIQUEFICATION OF GASES

Liquefication of gases : Boyle temperature and inversion temperature, Principle of regenerative cooling and of cascade cooling, liquefaction of hydrogen and helium.

Transport phenomena in gases : molecular collision, mean free path and collision cross sections. Estimates of molecular diameter and mean free path, Transport of mass, momentum and energy and inter relationship, dependence on temperature and pressure.

CHAPTER-3 : THERMODYNAMICS

The law of thermodynamics. The Zeroth law, first law of thermodynamics, internal and energy as a state functions and other applications. Reversible and irreversible changes, Carnot Cycle and its efficiency, Carnot theorem and the Second law of thermodynamics. Different versions of the second law Entropy, principles of increase of entropy. The thermodynamics scale of temperature;

CHAPTER-4 : MAXWELL'S RELATIONS

Thermodynamic relationship : Thermodynamic variables; extensive and intensive Maxwell's general relationships, application to Joule-Thomson cooling and adiabatic cooling in a general system, Vander Waal gas, Clausius-Clapeyron heat equation Thermodynamic potentials and equilibrium of thermodynamical systems; relation with thermodynamical variables. Cooling due to adiabatic dimagnetization.

CHAPTER-5 : RADIATION

Black Body radiation : Pure temperature dependence, Stefan-Boltzman law, pressure of radiation. Spectral distribution of Black body radiation, Wein displacement law, Rayleigh-Jean's law. Planck's quantum postulates, Planck's law.

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KINETIC THEORY OF MATTER-I**STRUCTURE**

- Concept of an Ideal Gas
- Pressure exerted by an Ideal Gas
- Root-Mean-Square Speed
- Interpretation of Temperature
- Degree of Freedom
- Law of Equipartition of Energy
- Limitations of Ideal Gas Equation
 - Student Activity
- Brownian Motion
- Equation of State
- Joule-Thomson (Kelvin) Effect
- Expression for Joule-Thomson Cooling
 - Summary
 - Student Activity
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Equation of state of an ideal gas, internal energy of an ideal gas.
- Basic assumptions and derivation for pressure of gas.
- Relation between rms speed and molecular weight; application in separation of isotopes.
- Calculation of molar specific heat and ratio of specific heat for monoatomic, diatomic and polyatomic gases.
- Explanation by van der Waal's equation, short coming of van der Waal's equation and law of corresponding states.
- External work done by a van der Waal's gas in isothermal expansion.
- Determination of Avogadro's number.
- Expressions for critical constants in terms of 'a' and 'b'.
- Porous Plug experiment; Joule expansion and Joule-Thomson expansion.

• 1.1. CONCEPT OF AN IDEAL GAS

From experiment, it is found that at low pressure all gases exhibit a certain simple relationship among the variables P , V and T . A gas for which this relationship remains same under all conditions, is called an ideal or perfect gas.

Let P , V and T be the pressure, volume and temperature of a 'real' gas.

From Boyle's law

$$P \propto \frac{1}{V} \quad (\text{constant } T)$$

$$PV = \text{constant}$$

From Charle's law

$$\frac{V}{T} = \text{constant}$$

Ideal gas equation follows these laws at all pressures. This means that all real gases approach an ideal gas at low pressure.

(a) **Equation of State of an Ideal Gas** : Let P_i, V_i, T_i, P_f and V_f, T_f be the initial and final pressure, volume and temperature respectively of a given mass of an ideal gas.

Consider the change to take place in two stages :

(i) Let at constant temperature T_i , an increase in the pressure be from P_i to P_f . Let during this process the volume change to some value V .

From Boyle's law

$$P_i V_i = P_f V$$

or

$$V = \frac{P_i V_i}{P_f} \quad \dots(1)$$

(ii) And an increase in the temperature of this volume of gas from T_i to T_f , the pressure remaining constant at P_f . The volume changes from V to V_f and by Charle's law

$$\frac{V}{T_i} = \frac{V_f}{T_f}$$

or

$$V = \frac{V_f T_i}{T_f} \quad \dots(2)$$

From equations (1) and (2), we get

$$\frac{P_i V_i}{P_f} = \frac{V_f T_i}{T_f}$$

or

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \quad \dots(3)$$

$$\frac{PV}{T} = \text{constant} \quad \dots(4)$$

Since at a given pressure and temperature, the volume occupied by a gas is proportional to its mass and constant involved in equation (4) must also be proportional to the mass of the gas. Let us write this constant as μR where μ is the mass of the gas in gram molecules and R is a constant. Then equation (4) reduces to

$$PV = \mu RT \quad \dots(5)$$

It is found that at low pressure, R has the same value for all gases and it is called the 'universal gas constant'.

The equation (5) is known as the equation of state of an ideal gas.

For one gram molecule of an ideal gas $\mu = 1$, therefore

$$PV = RT$$

for one gram of the gas $R = r$, then

$$PV = rT$$

where r is the gas constant for 1 gram of the gas. It is not a universal constant and varies from gas to gas as $r = \frac{R}{M}$, where M is the molecular weight of the gas.

(b) **Internal Energy of an Ideal Gas** : The molecules of an ideal gas do not exert force of attraction on each other, i.e., potential energy will be zero. Hence, the internal energy of an ideal gas is entirely kinetic which depends upon the temperature only and is independent of the volume. This is called 'Joule's law'.

(c) **Calculation of Gas Constant R** : From equation (5), we have

$$R = \frac{PV}{\mu T} \quad \dots(6)$$

For one mole of an ideal gas at N.T.P., we have,

$$P = 1.013 \times 10^5 \text{ newton /metre}^2$$

$$V = 22.4 \text{ litre} = 22.4 \times 10^{-3} \text{ metre}^3$$

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

$$\mu = 1 \text{ mole}$$

Putting these values in equation (6), we get

$$R = \frac{1.013 \times 10^5 \times 22.4 \times 10^{-3}}{1 \times 273}$$

$$= 8.31 \text{ joule / (mole-K)}$$

• 1.2. PRESSURE EXERTED BY AN IDEAL GAS

When a certain amount of ideal gas is confined in a closed vessel, then the molecules collide with the walls and come back after reflection. During the collision, each molecule suffers a change in momentum. According to Newton's second law of motion, the rate of change of momentum is equal to the force exerted and this force per unit surface area of the walls is the pressure of the gas.

(a) **Basic Assumptions** : For calculating the pressure of the gas, the following assumptions are made :

(i) The molecules of a gas are hard, smooth and spherical in shape.

(ii) The time of collision is negligible in comparison to the time taken to traverse the free path.

(iii) The collisions between molecules and walls are perfectly elastic so that there is no loss of kinetic energy in the collision.

(iv) The molecules exert no force on each other except when they collide and whole of the molecular energy is kinetic.

(v) The size of the molecules is very small. Hence the volume of a molecule is negligible in comparison to the total volume of the gas.

(vi) The intermolecular distance in a gas is much larger than that of a solid or liquid and the molecules of a gas are free to move in the entire space available to them.

(b) **Derivation for Pressure of Gas** : Let us consider an ideal gas filled in cubical vessel of side l . Let n be the total number of molecules in a gas and m be the mass of each molecule. Let one of the molecules move with velocity \vec{v}_1 in any direction towards the face A as shown in fig. 1.

The components of velocity \vec{v}_1 are v_{1x} , v_{1y} and v_{1z} , respectively *i.e.*,

$$v_1^2 = v_{1x}^2 + v_{1y}^2 + v_{1z}^2$$

Since the collision is perfectly elastic, therefore this particle strikes the face A with a velocity \vec{v}_1 and reflects with the same velocity. Since the face A is perpendicular to x -axis, therefore only the v_{1x} component will be affected.

The momentum of the molecule along x -direction before collision

$$= mv_{1x}$$

The momentum of the molecule along x -direction after collision

$$= -mv_{1x}$$

The change in momentum during one collision along x -axis

$$= mv_{1x} - (-mv_{1x})$$

$$= 2mv_{1x}$$

The molecules, after reflection, strike the face A' opposite to A , and travel again to A after covering a distance $2l$ with the same velocity v_{1x} . Therefore, the time taken by the molecule between two successive collisions on the face A

$$= \frac{2l}{v_{1x}}$$

\therefore Number of collisions per second

$$= \frac{v_{1x}}{2l}$$

Hence the change in momentum per second due to the collision of the molecule again face

$$= 2mv_{1x} \times \frac{v_{1x}}{2l}$$

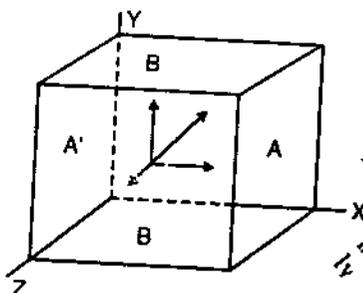


Fig. 1

$$= \frac{mv_{1x}^2}{l}$$

for n molecules, the net change in momentum per second due to all the molecules striking the face A

$$= \frac{mv_{1x}^2}{l} + \frac{mv_{2x}^2}{l} + \dots + \frac{mv_{nx}^2}{l}$$

$$= \sum_{i=1}^n \frac{mv_{ix}^2}{l}$$

where $v_{1x}, v_{2x}, \dots, v_{nx}$ are the components of the velocities of all the n molecules.

According to Newton's second law, this rate of change of momentum is equal to the force exerted by the gas, *i.e.*,

$$\text{Net force of the gas on face } A = \frac{m}{l} \sum_{i=1}^n v_{ix}^2$$

The pressure on the surface A is

$$P_x = \frac{\text{force}}{\text{area}}$$

or

$$P_x = \frac{m}{l \cdot l^2} \sum_{i=1}^n v_{ix}^2$$

or

$$P_x = \frac{m}{V} \sum_{i=1}^n v_{ix}^2 \quad \dots(1)$$

where V is the volume of the cube.

Similarly, the pressures P_y and P_z exerted on the other two faces B and C perpendicular to y and z axes respectively, are

$$P_y = \frac{m}{V} \sum_{i=1}^n v_{iy}^2 \quad \dots(2)$$

and

$$P_z = \frac{m}{V} \sum_{i=1}^n v_{iz}^2 \quad \dots(3)$$

When the cubic vessel is small, the gravity does not play any role. The pressure on all the faces is same in all directions, *i.e.*,

$$P_x = P_y = P_z = P \quad (\text{say}) \quad \dots(4)$$

\therefore

$$P = \frac{1}{3} (P_x + P_y + P_z)$$

From equations (1), (2) and (3)

$$P = \frac{1}{3} \frac{m}{V} \left[\sum_{i=1}^n v_{ix}^2 + \sum_{i=1}^n v_{iy}^2 + \sum_{i=1}^n v_{iz}^2 \right]$$

$$= \frac{1}{3} \frac{m}{V} \sum_{i=1}^n (v_{ix}^2 + v_{iy}^2 + v_{iz}^2)$$

$$= \frac{1}{3} \frac{m}{V} \sum_{i=1}^n v_i^2 \quad \dots(5)$$

where $v_i^2 = v_{ix}^2 + v_{iy}^2 + v_{iz}^2$

Mean square speed is given by

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{N}$$

$$= \frac{\sum_{i=1}^n v_i^2}{N}$$

$$\text{or } \sum_{i=1}^n v_i^2 = N \bar{v}^2 \quad \dots(6)$$

From equations (5) and (6), we get

$$P = \frac{1}{3} \frac{m}{V} n \bar{v}^2$$

But $mN = M =$ total mass of the gas

$$P = \frac{1}{3} \frac{M}{V} \bar{v}^2 = \frac{1}{2} \rho \bar{v}^2$$

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

$$\text{Thus, } P = \frac{2}{3} \left(\frac{1}{2} \rho \bar{v}^2 \right)$$

$$P = \frac{2}{3} E$$

where $E = \frac{1}{2} \rho \bar{v}^2$ is the kinetic energy per unit volume of the gas. **Thus, the pressure of the gas is equal to two-thirds of the total translational kinetic energy of the molecules per unit volume.**

• 1.3. ROOT-MEAN-SQUARE SPEED

All the gases consist of a large number of small particles. These particles are known as molecules. These molecules move constantly in a straight line in all directions. It is found that all the molecules do not move with the same speed, but the speeds are distributed about an average value which depends upon the temperature of the gas. The collision between molecules takes place. Due to this, the speeds change but according to Maxwell, the number of molecules having speed between the given range remains constant.

Let $v_1, v_2, v_3 \dots v_n$ be the speeds of n molecules of the gas, then mean-square-speed of the molecules is

$$\bar{v}^2 = \frac{v_1^2 + v_2^2 + \dots + v_n^2}{N}$$

from kinetic theory, the pressure exerted by an ideal gas is

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

or

$$\bar{v}^2 = \frac{3P}{\rho}$$

or

$$\sqrt{\bar{v}^2} = v_{rms} = \sqrt{\frac{3P}{\rho}} \quad \dots(1)$$

where $\sqrt{\bar{v}^2}$ is known as root-mean-square speed of the gas molecule.

The speed of sound in gas is given by Laplace's formula, *i.e.*,

$$v = \sqrt{\frac{\gamma P}{\rho}} \quad \dots(2)$$

From equations (1) and (2), we get

$$v \propto v_{rms}$$

or

$$\frac{v_1}{v_2} = \frac{v_{1,rms}}{v_{2,rms}}$$

(b) Relation between r.m.s. Speed and Molecular Weight : For 1 mole of a gas, the density

is

$$\rho = \frac{M}{V} \quad \dots(3)$$

where M is the molecular weight and V is the volume.

$$\text{But } PV = RT \quad \dots(4)$$

from equations (3) and (4), we get

$$\frac{P}{\rho} = \frac{RT}{M}$$

Putting this value in equation (1), we get

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

from this expression, it is clear that the rms speed of the molecules of an ideal gas is inversely proportional to the square root of the molecular weight of the gas.

But $M = mN$, where m is the mass of a single molecule and N is the Avogadro's number *i.e.*, number of molecules per mole of a gas. Thus,

$$v_{rms} = \sqrt{\frac{3RT}{mN}} = \sqrt{\frac{3KT}{m}}$$

where $K \left(= \frac{R}{N} \right)$ is the Boltzman constant, From this expression, we see that

$$v_{rms} \propto \sqrt{\frac{1}{m}}$$

or

$$\frac{v_{1rms}}{v_{2rms}} = \sqrt{\frac{m_2}{m_1}}$$

This means that, at constant temperature the ratio of the root-mean-square speed of molecules of two different gases is equal to the square-root of the inverse ratio of their masses.

Application in Separation of Isotopes :

The above relation has the important application for the diffusion of two different gases through the porous walls of a container. **The lighter gas whose molecules have a larger speed, would escape faster than the heavier gas.** The diffusion process is used to separate the lighter isotope from a normal specimen of a material.

The ordinary uranium contains a lighter isotope U^{235} (0.7%) and a heavier isotope U^{238} (99.3%). The lighter isotope U^{235} is very useful in making atom bomb because its nucleus can be fissioned easily. Hence U^{235} must be separated from ordinary uranium. When the uranium is diffused through the porous walls of a container, then U^{235} is separated out.

(c) **Air leaking into vacuum is richer in H_2 and He :** H_2 and He are much lighter in comparison to N_2 , O_2 etc. which are found in air and hence H_2 and He have larger root-mean-square speed. This means that they leak faster.

(d) **Time for Diffusion-Separation :** When two gases are to be separated from a mixture by diffusion then a number of successive diffusion stages are used and the diffusion time in each stage being small. If time would be long then both gases will ultimately diffuse out and separation would not be possible.

• 1.4. INTERPRETATION OF TEMPERATURE

According to Maxwell's dynamic theory of gas, the average kinetic energy of translation of the molecules of an ideal gas is directly proportional to its absolute temperature.

Consider 1 gram molecule of a gas at absolute temperature T filled in a vessel of volume V . According to kinetic theory, the pressure of a gas is

$$P = \frac{1}{3} \frac{mN}{V} \bar{v}^2 \quad \dots(1)$$

where N is the Avogadro number, m is the mass of a molecule and \bar{v}^2 is the mean square speed.

From equation (1),

$$\begin{aligned} PV &= \frac{1}{3} mN \bar{v}^2 \\ &= \frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2 \right) \end{aligned} \quad \dots(2)$$

The ideal gas equation is

$$PV = RT \quad \dots(3)$$

where R is gas constant From equations (2) and (3), we get

$$\frac{2}{3} N \left(\frac{1}{2} m \bar{v}^2 \right) = RT$$

or

$$\begin{aligned} \frac{1}{2} m \bar{v}^2 &= \frac{3}{2} \frac{R}{N} T \\ &= \frac{3}{2} kT \end{aligned} \quad \dots(4)$$

where $k = \frac{R}{N}$ is a constant and this constant is known as Boltzmann's constant.

($k = 1.38 \times 10^{-23}$ joule /K).

From equation (4), it is clear that **the average kinetic energy of translation of molecule $\left(\frac{1}{2} m \bar{v}^2 \right)$ is directly proportional to the absolute temperature of the gas.**

When the temperature of a gas increases, then the average kinetic energy of the gas increases and vice-versa. Thus, average kinetic energy of translation of the molecules is the measurement of the temperature.

From equation (4),

$$\bar{v}^2 = \frac{3kT}{m} \quad \dots(5)$$

At $T = 0$,

$$\bar{v}^2 = 0$$

The root-mean-square speed is given by

$$v_{rms} = \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}}$$

or

$$v_{rms} \propto \sqrt{T} \quad \dots(6)$$

Hence, according to the kinetic interpretation of temperature, the kinetic energy of the gas molecules should be zero at absolute zero temperature. This means that, absolute zero is that temperature at which all molecular motions of a gas cease.

• 1.5. DEGREE OF FREEDOM

The degree of freedom of a particle is the total number of independent motions possible for it or the number of independent coordinates required to specify its dynamic position.

In monoatomic gases (like helium, argon), the molecule consists of only one atom. Therefore molecule can be expressed as a point in space without assigning any internal structure to it. This means that, there will be only translatory motion and its translational motion can take place in any direction in space which can easily be resolved along three mutually perpendicular axes X , Y and Z as shown in the fig. 2(i). Thus it can have three independent motions and hence three degrees of freedom.

The molecule of a diatomic gas (like hydrogen, oxygen etc.) is made up of two atoms joined rigidly to one another like a dumb bell as shown in fig. 2(ii). Such a molecule, besides its translatory motion can rotate about any three mutually perpendicular axes. However, the rotational inertia about an axis along the rigid rod will be negligible in comparison to those about the other two axes, so

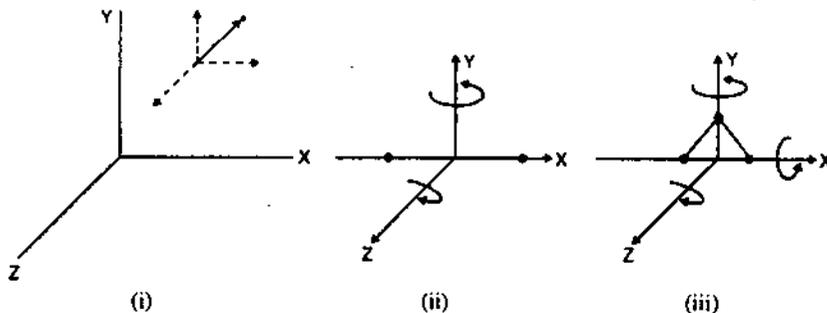


Fig. 2.

that the rotational energy would consist of only two terms such as $\frac{1}{2} I \omega_y^2$ and $\frac{1}{2} I \omega_z^2$. Hence it can have only two rotational motions. Thus a diatomic molecule has five degrees of freedom, Three translational and two rotational.

A polyatomic molecule (like carbon dioxide) can rotate about three mutually perpendicular axes as shown in fig. 2(iii). Thus it possesses six degrees of freedom—three translational and three rotational.

If we consider the vibrations of atoms in diatomic and polyatomic molecules then the molecule possesses still more degrees of freedom.

• 1.6. LAW OF EQUIPARTITION OF ENERGY

According to this law "the total internal energy of a dynamical system consisting of a large number of particles (like molecules of a gas) is equally divided among all its degrees of freedom and the average energy per particle associated with each degree of freedom is $\frac{1}{2} kT$, where k is Boltzmann's constant and T is the absolute temperature of the system in equilibrium.

(a) Calculation of Molar Specific Heat and Ratio of Specific Heat for Monoatomic, Diatomic and Polyatomic Gases : Let us consider one gram molecule of an ideal gas at absolute temperature T . The average kinetic energy per molecule will be $\frac{1}{2} nkT$ where n is the number of degrees of freedom. Since in ideal gas, there is no force of attraction between the molecules except during collisions the potential energy will be zero and the total internal energy will be kinetic.

If N is Avogadro's number, then the internal energy of 1 gram molecule of an ideal gas is

$$U = N \cdot \frac{1}{2} nkT = \frac{1}{2} n(Nk)T$$

or

$$U = \frac{1}{2} nRT \quad \dots(1)$$

where $R = Nk$, is the gas constant.

Differentiating equation (1), with respect to T , we get

$$\frac{dU}{dT} = \frac{1}{2} nR \quad \dots(2)$$

Let the gas be heated at constant volume until its temperature rises by dT . In this position, the heat supplied would be $C_v dT$. Since volume remains constant, therefore no work is done.

Hence from first law of thermodynamics

$$dQ = dU + dW$$

$$C_v dT = dU + 0$$

$$C_v = \frac{dU}{dT} \quad \dots(3)$$

From equations (2) and (3), we get

$$\boxed{C_v = \frac{1}{2} nR} \quad \dots(4)$$

This is the molar specific heat of the gas at constant volume.

We know that

$$C_p - C_v = R$$

where C_p is the molar specific heat at constant pressure.

$$C_p = C_v + R$$

$$= \frac{1}{2} nR + R$$

$$C_p = \left(\frac{n}{2} + 1 \right) R$$

Therefore,

$$\frac{C_p}{C_v} = \gamma = \frac{\left(\frac{n}{2} + 1 \right) R}{\frac{n}{2} R}$$

or

$$\gamma = \frac{C_p}{C_v} = 1 + \frac{2}{n} \quad \dots(5)$$

From this it is clear that γ decreases with increase in degree of freedom (n).

(b) Monoatomic Gases : For this, the degree of freedom will be three, *i.e.*, $n = 3$.

Therefore, $C_v = \frac{1}{2} nR = \frac{3}{2} R = 3 \text{ cal /mole-K}$ [$\because R = 2 \text{ cal /mole-K}$]

$$C_p = \left(\frac{n}{2} + 1 \right) R = \frac{5}{2} R = 5 \text{ cal /mole-K}$$

and

$$\gamma = 1 + \frac{2}{n} = 1 + \frac{2}{3} = \frac{5}{3} = 1.66$$

Since, the specific heat C_v and C_p are independent of gas temperature, therefore the molar specific heat of all monoatomic gases are the same at all temperatures. It is also found that the experimental value of C_v , C_p and γ for all the inert and other monoatomic gases agree with the above theoretical values.

(c) Diatomic Gases : The molecule of a diatomic gas has 5 degrees of freedom, 3 translational and 2 rotational, *i.e.*, $n = 5$. Thus,

$$C_v = \frac{n}{2} R = \frac{5}{2} R \approx 5 \text{ cal /mole-K}$$

$$C_p = \left(\frac{n}{2} + 1 \right) R = \frac{7}{2} R \approx 7 \text{ cal /mole-K}$$

$$\gamma = 1 + \frac{2}{n} = 1 + \frac{2}{5} = \frac{7}{5} = 1.40$$

For many diatomic gases (like H_2 , O_2 etc.), the experimental value of C_v , C_p and γ is in close agreement with these theoretical values, but in some cases, there is disagreement. Because for C_2 , the values of C_v and C_p are higher and of γ lower than the theoretical values.

(d) Triatomic Gases : A molecule of triatomic gas has 6 degrees of freedom—3 translational and 3 rotational, *i.e.*, $n = 6$. Thus

$$C_v = \frac{n}{2} R = 3R = 6 \text{ cal /mole-K}$$

$$C_p = \left(\frac{n}{2} + 1 \right) R = 4R = 8 \text{ cal /mole-K}$$

$$\gamma = 1 + \frac{2}{n} = 1 + \frac{2}{6} = \frac{8}{6} = 1.33$$

In this case of triatomic gas, a large difference is obtained between theoretical and experimental values, *i.e.*, the experimental values of C_p and C_v are larger than the theoretical values while γ is smaller.

• 1.7. LIMITATIONS OF IDEAL GAS EQUATION

The limitation of ideal gas equation is that it applies to real gases at low pressure and high temperature only.

Explanation by van der Waals' Equation

From the ideal gas equation $PV = RT$, we see that the product PV should remain constant at constant temperature. Hence the curves between PV and P should be parallel to the pressure-axis. But in fact it is not so. Hence the equation $PV = RT$ does not hold good for a real gas. This difficulty was removed by the van der Waal's equation. The van der Waals' equation is

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

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$PV = RT + Pb - \frac{a}{V} + \frac{ab}{V^2}$$

Since the terms $\frac{a}{V}$ and $\frac{ab}{V^2}$ are very small, so we can replace

$\frac{P}{RT}$ by $\frac{1}{V}$, then

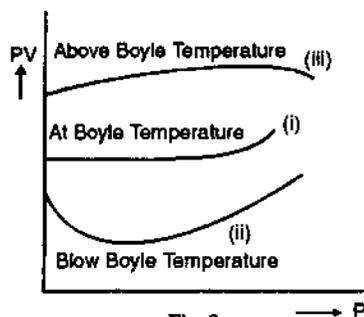


Fig. 3

$$PV = RT + Pb - \frac{ap}{RT} + \frac{abp^2}{R^2T^2}$$

or

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

At low pressure, the term $\frac{abp^2}{R^2T^2}$ can be neglected. Hence

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

At low temperature $\left(b - \frac{a}{RT} \right)$ will be negative. Therefore PV decreases on increasing P . But if P increases then the term $\frac{abp^2}{R^2T^2}$ becomes more significant and beyond a particular value of P , the product PV begins to increase with P . This explains the lowest curve of fig. 3.

At high temperature, $\frac{a}{RT}$ becomes small so that the term $\left(b - \frac{a}{RT} \right)$ is positive. Hence PV increases with increase in p . This explains the upper curve of fig. 3.

If $b - \frac{a}{RT} = 0$ or $T = \frac{a}{bR}$, then PV remains constant. This is the "Boyle temperature" T_B . This explains the middle curve of fig. 3. Thus

$$T_B = \frac{a}{bR}$$

This is the relationship between Boyle temperature and van der Waals' constants.

(b) Short coming of van der Waals' Equation : The van der Waals' equation of state is

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

This equation is an accurate representation of the behaviour of real gases. But the constants a and b are different for different gases. This difficulty is removed by 'reduced equation of state'.

(c) Reduced Equation of State : Let P, V, T be actual pressure, volume and temperature of a gas and P_c, V_c, T_c be the critical pressure, volume and temperature. Then $\frac{P}{P_c}, \frac{V}{V_c}, \frac{T}{T_c}$ are known as reduced pressure P_r , reduced volume V_r and reduced temperature T_r , respectively. Thus,

$$P = P_r P_c$$

$$V = V_r V_c$$

and

$$T = T_r T_c$$

Putting these values in van der Waals' equation, we get

$$\left(P_r P_c + \frac{a}{V_r^2 V_c^2} \right) (V_r V_c - b) = RT_r T_c$$

$$\text{But } P_c = \frac{a}{27 b^2}, V_c = 3b, T_c = \frac{8a}{27 bR}$$

$$\therefore \left(P_r \frac{a}{27 b^2} + \frac{a}{9 V_r^2 b^2} \right) (3V_r b - b) = RT_r \frac{8a}{27 bR}$$

or

$$\frac{a}{27 b^2} \left(P_r + \frac{3}{V_r^2} \right) b (3V_r - 1) = 8 T_r \frac{a}{27 b}$$

or

$$\left(P_r + \frac{3}{V_r^2} \right) (3V_r - 1) = 8 T_r$$

This equation is known as van der Waals' **reduced equation of state**. Since this equation of state is independent of the constants a and b , hence it holds for any van der Waals' gas.

(d) Law of Corresponding States : According to this law, "When two of the three quantities P_r, V_r and T_r are the same for any two gases, then the third quantity will also be the same for those two gases". This is the **law of corresponding states**.

(e) **External Work done by a van der Waals' Gas in Isothermal Expansion :** Suppose 1 mole of a van der Waals' gas at temperature T is expands isothermally from an initial volume V_i to the final volume V_f , then work done by it is

$$W = \int_{V_i}^{V_f} P dV$$

But for van der Waals' gas

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

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$W = \int_{V_i}^{V_f} \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) dV$$

$$= RT \left[\log_e (V - b) \right]_{V_i}^{V_f} + a \left[\frac{1}{V} \right]_{V_i}^{V_f}$$

$$= RT \log_e \frac{V_f - b}{V_i - b} + a \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$$

For μ moles

$$W = \mu RT \log_e \frac{V_f - \mu b}{V_i - \mu b} + a\mu^2 \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$$

This is the desired result.

• STUDENT ACTIVITY

1. Find out the value of gas constant R .

2. What do you mean by degree of freedom ?

3. What is the limitation of ideal gas equation ?

• 1.8. BROWNIAN MOTION

This phenomenon was first discovered by an English botanist Brown in 1827. He found that pollen suspended in water shows a continuous random motion, when viewed under a microscope. He found the spores dancing about in a state of random motion. This phenomenon was most clear in case of colloidal solutions. The suspended particles appear moving to and fro, rapidly and continuously in an entirely random way. This irregular motion is known as 'Brownian motion' of the particle.

Explanation from Kinetic Theory : This phenomenon was explained by Einstein on the basis of kinetic theory. According to him, the particle suspended in a fluid takes part in the thermal motion of the molecules of the fluid. These particles are continuously affected by the molecules of the fluid. Since the particles are very small in size, so the number of molecules striking them on opposite sides are not always exactly balanced. This means that a particle always experiences an **unbalanced** force and is continuously driven about in random directions. Thus, these particles behave as 'large' molecules of the fluid.

Determination of Avogadro's Number : French chemist Perrin found that the colloidal particles suspended in a liquid behave like a gas. Therefore their density varies with height in the liquid in the same way as the pressure of the atmosphere varies with altitude.

Consider a small element of the gas at height h from the bottom as shown in fig 4. Let A and dh be the face area and thickness of the gas element, respectively.

If P is the density of the gas at height h then the mass of the element is ρAdh and its weight is $\rho g Adh$.

Let P be the pressure on the lower face acting in upward direction and $p + dp$ that on the upper face of the element acting in downward direction. Hence the upward force acting on the element is PA , and the downward force is $(P + dp) A$. If the element is in equilibrium, then

$$PA = (P + dp) A + \rho g Adh$$

or

$$dp = -\rho g dh \quad \dots (1)$$

From

$$PV = RT$$

But $V = \frac{M}{\rho}$ where M is the molecular weight of the gas. If m be the mass of a gas molecule and N the Avogadro's number, then $M = mN$, thus

$$V = \frac{mN}{\rho}$$

$$\therefore P \frac{mN}{\rho} = RT$$

$$\text{or } P = \frac{\rho RT}{mN}$$

From equation (1), we get

$$\frac{dp}{P} = -\frac{mNg}{RT} dh$$

Let at bottom (at $h = 0$), the pressure be P_0 . Then integrating between the limits $p = p_0$ to $p = p$, and $h = 0$ to $h = h$, we get

$$\int_{p_0}^p \frac{dP}{P} = -\frac{mNg}{RT} \int_0^h dh$$

$$\log_e \frac{P}{P_0} = -\frac{mNg}{RT} h$$

$$\frac{P}{P_0} = e^{-\frac{mNgh}{RT}}$$

$$\therefore P = P_0 e^{-\frac{mNgh}{RT}}$$

Since the pressure of a gas is proportional to the number of molecules per unit volume of the gas, therefore above expression can be written as

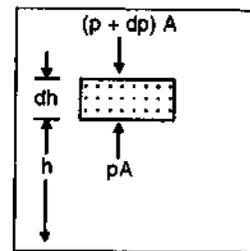


Fig. 4

$$n = n_0 e^{-\frac{mNgh}{RT}}$$

where n is the number of molecules per unit volume at height h and n_0 that at the bottom.

If the buoyancy effect is taken into consideration, then the effective mass m of the particle would be $V(\rho - \rho')$, where V is the volume of a particle, ρ the density of particles and ρ' the density of the liquid. Then

$$n = n_0 e^{-NV(\rho - \rho')gh/RT}$$

or

$$N = \frac{RT}{V(\rho - \rho')gh} \log_e \frac{n_0}{n}$$

By this expression we can calculate the Avogadro's number. Perrin obtained a value $N = 6.8 \times 10^{23}$ particles /mole.

• 1.9. EQUATION OF STATE

No real gas obeys the gas laws perfectly. At ordinary pressure and temperature, the deviation is small but at high pressure and low temperature, the deviations are very large. Therefore the ideal gas equation $PV = RT$ does not correctly represent the behaviour of real gases. The deviation of ideal gas equation is based on the following two assumptions :

- (i) The molecules of a gas are infinitesimally small in size, *i.e.*, they have no finite volume.
- (ii) The molecules do not exert force of attraction or repulsion between the molecules.

Actually, the molecules of real gases possess a finite size and also attract one another. Due to this fact, the equation of state of an actual gas is different from that of an ideal gas.

(b) van der Waal's Equation of State. van der Waal modified the ideal gas equation by considering the finite size of molecules and their mutual attraction.

The equation of state for one gram molecule of the ideal gas occupying a volume V at a pressure P is

$$PV = RT \quad \dots(1)$$

Now, let us apply the following corrections to 1 gram molecule of an actual gas having an observed volume v at an observed pressure p .

(i) Correction for finite size of molecules. If the molecules possess a finite size, the space available for the molecules to move about is less than the observed volume. Let a molecule be moving between the two walls CF and DE of the container as shown in fig. 5.

In one complete trip from CF to DE and again to CF the distance travelled by the molecule is not $2L$ but $(2L - d)$, where d is the diameter of the molecule. In this way, considering the motion of all these molecules the effective volume in which they are moving is less than the total volume V . Hence the reduction in volume can be

brought about by subtracting a correctional term b from the measured volume, *i.e.*, $(V - b)$ should be used in place V . Thus,

$$V_i = (v - b) \quad \dots(2)$$

where b is a constant, called the "covolume" for 1 gram molecule of the gas. The value of ' b ' is found to be four times the actual volume of the molecules of gas.

(ii) Correction for molecular attraction : Consider a molecule A in the interior of the gas as shown in fig. 6. It is surrounded by other molecules equally distributed in all directions. The resultant pull is zero because various forces merely cancel each other. But a molecule B near the wall of the vessel is subject to an inward pull due to unbalanced forces. In this case components parallel to the wall are cancelled and perpendicular components are directed inwards. Obviously, this inward pull on the particle reduces the momentum with which the molecule strikes the wall.

It is observed that the decrease in pressure is proportional to the product of the force on a molecule due to the molecules attracting it and number of molecules striking unit area of wall per second. Each of these factors depends upon the number of molecules in unit volume of the gas or the density of the gas, hence

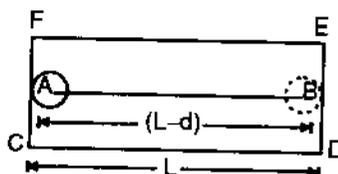


Fig. 5

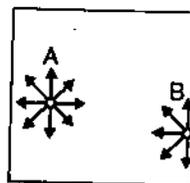


Fig. 6

decrease in pressure \propto (density of gas)²

$$\propto \frac{1}{V^2} = \frac{a}{V^2},$$

where a is constant for 1 gram molecule of the gas.

The term $\frac{a}{V^2}$ is known as the **internal pressure**.

Therefore we should use $\left(p + \frac{a}{V^2}\right)$ instead of p in the equation of state

$$\text{i.e.,} \quad P_i = p + \frac{a}{V^2} \quad \dots(3)$$

Thus substituting V and P , equation of state assumes the form

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

This is known as van der Waal's equation of state for 1 mole of gas. For μ moles of gas, the equation can be written as

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

(c) **Expressions for critical constants in terms of 'a' and 'b'.** The three critical constants of a gas are :

- (i) the critical temperature T_c ,
- (ii) the critical pressure p_c , and
- (iii) the critical volume, V_c

To determine their values, the van der Waal's equation can be written as

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \quad \dots(1)$$

When p is plotted against v at different temperatures T , the curves in the form of isotherms are obtained (fig. 7). Isotherms below the critical point P have minima and maxima. The positions can be obtained by differentiating equation (1) w.r.t. V and then equating to zero. That is

$$\left(\frac{dp}{dV}\right)_T = 0 \quad \dots[2 (i)]$$

$$\text{and} \quad \left(\frac{d^2p}{dV^2}\right)_T = 0 \quad \dots[2 (ii)]$$

Let us apply the first condition 2 (i) to van der Waal's equation (1), we get

$$\left(\frac{dp}{dV}\right)_T = -\frac{RT}{(V - b)^2} + \frac{2a}{V^3} = 0 \quad \dots(3)$$

Putting this value of $\frac{RT}{V - b}$ in equation (1), we shall get an equation which would represent a curve which passes through the maxima and minima of the isotherms.

Now applying second condition 2 (ii) to van der Waal's equation (1), we get

$$\left(\frac{d^2p}{dV^2}\right)_T = \frac{2RT}{(V - b)^3} - \frac{6a}{V^4} = 0 \quad \dots(4)$$

At the critical point, $V = V_c$, $P = P_c$ and $T = T_c$. Hence equations (1), (3) and (4) can be written in the following form

$$P_c = \frac{RT_c}{V_c - b} - \frac{a}{V_c^2} \quad \dots(5)$$

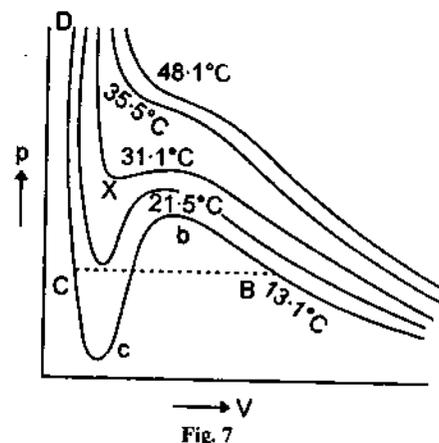


Fig. 7

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

and

$$\frac{2RT_c}{(V_c - b)^3} = \frac{6a}{V_c^4} \quad \dots(7)$$

For critical volume. Now divide equation (6) by eqn. (7), we get

$$\frac{1}{2}(V_c - b) = \frac{1}{3}V_c$$

$$\Rightarrow V_c = 3b \quad \dots(8)$$

For critical temperature. Putting the value of V_c in eqn. (6), we have

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

$$\Rightarrow T_c = \frac{8a}{27bR} \quad \dots(9)$$

For critical pressure. Now substitute the values of V_c and T_c in eqn. (5), we have

$$P_c = \frac{R}{2b} \left(\frac{8a}{27bR} \right) - \frac{a}{9b^2}$$

$$\Rightarrow \boxed{P_c = \frac{a}{27b^2}} \quad \dots(10)$$

For critical coefficient. The expression $\frac{RT_c}{P_c V_c}$ is known as the "critical coefficient" whose value can be found out by substituting the values of V_c , T_c and P_c from eqns. (8), (9) and (10). That is

$$\frac{RT_c}{P_c V_c} = \frac{R}{27bR} \frac{8a}{a} \left(\frac{27b^2}{3b} \right) \frac{1}{3b} = \frac{8}{3} = 2.67$$

This value is same for all gases.

Determination of 'a' and 'b'. The values of the constants 'a' and 'b' can be determined in terms of critical pressure P_c and critical temperature T_c . Thus from eqns. (9) and (10), we have

$$\frac{T_c^2}{P_c} = \left(\frac{8a}{27bR} \right)^2 \frac{27b^2}{a} = \frac{64}{27R^2}$$

$$\Rightarrow \boxed{a = \frac{27R^2}{64} \left(\frac{T_c^2}{P_c} \right)} \quad \dots(11)$$

Further using eqns. (9) and (10) as

$$\frac{T_c}{P_c} = \frac{8a}{27bR} \times \frac{27b^2}{a} = \frac{8b}{R}$$

$$\Rightarrow b = \frac{R}{8} \left(\frac{T_c}{P_c} \right) \quad \dots(12)$$

Thus the values of 'a' and 'b' can be determined if the values of T_c and P_c are known.

To determine the value of T_c and P_c for ordinary substance, the liquid is introduced into a hard glass tube connected to a manometer. The hard glass tube is then placed in a thermostat so that the substance can be raised to any known temperature. The temperatures at which the liquid meniscus disappears and reappears are observed. The mean of these two temperatures gives the critical temperature T_c . The pressure recorded by the manometer at the critical temperature is the critical pressure P_c . Knowing T_c and P_c values of 'a' and 'b' can be estimated.

• 1.10. JOULE-THOMSON (KELVIN) EFFECT

According to Joule-Thomson effect, "when a gas is passed from higher to lower pressure through a porous plug (cotton, wool etc.) then the gas shows a change in its temperature. This effect was demonstrated by Joule and Thomson. Hence it is known as Joule-Thomson (Kelvin) effect.

Porous Plug Experiment : The experimental arrangement is shown in the fig. 8. The gas is first compressed by the compressor and after passing through the spiral S , the gas attains the temperature of the bath C , which is measured with the help of the thermometer T_1 . The cooled gas enters the porous-plug G , which is kept in a wooden tube B . The tube B is filled with cotton wool, which acts as an insulator. The temperature of the gas after passing through the porous plug is measured with the help of the thermometer T_2 and pressure is of the gas is measured before and after passing through the porous-plug.

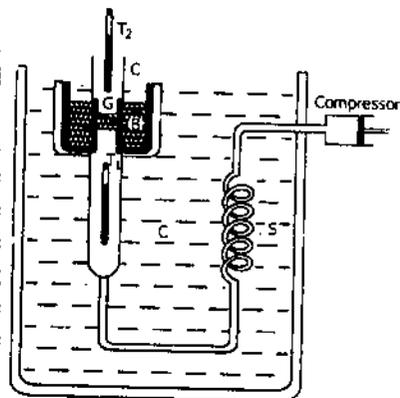


Fig. 8

Results : From the above experiment, the following results are obtained :

- (i) All gases suffer a change in temperature after passing through the porous-plug.
- (ii) The change in temperature is directly proportional to the pressure difference on both sides of the porous-plug.
- (iii) At ordinary temperatures, all gases except hydrogen and helium show cooling effect while hydrogen and helium show heating effect.
- (iv) The fall in the temperature (per atmosphere difference of pressure) decreased, if the initial temperature of the gas is increased and becomes zero at a particular temperature. Above this particular temperature the gas shows heating effect. The temperature at which Joule-Thomson effect changes *i.e.*, cooling effect becomes heating effect, is known as **temperature of inversion**. This temperature is different for different gases.

From above it is clear that *all gases below their temperature of inversion show cooling effect after passing through the porous-plug.*

Explanation of Results : Let us consider a narrow tube with porous-plug E . Two movable and frictionless pistons A and B are attached to it. When the piston is compressed, the gas reaches in right compartment from left compartment. The piston is so moved that the high pressure in left side and low pressure on the right side are constant.

Let P_1 , V_1 and T_1 be its pressure, volume and temperature respectively before passing through the porous-plug and P_2 , V_2 and T_2 similar quantities after passing through the porous-plug. Let U_1 and U_2 be the internal energies of the gas before and after passing through the porous-plug.

$$\text{Work done on the gas by the piston } A = P_1 V_1$$

$$\text{Work done by the gas on the piston } B = P_2 V_2$$

$$\text{Net work done by the gas} = P_2 V_2 - P_1 V_1$$

To do this work, the gas takes required energy from itself.

$$\text{i.e.,} \quad P_2 V_2 - P_1 V_1 = U_1 - U_2$$

$$\text{or} \quad P_1 V_1 + U_1 = P_2 V_2 + U_2$$

$$\text{or} \quad U + PV = \text{constant}$$

The quantity $U + PV$ is known as 'enthalpy' H . Hence, in Joule-Thomson effect the enthalpy remains constant, *i.e.*, enthalpy of the gas before and after passing through porous-plug is equal.

The internal energy of the gas consists of two parts :

- (i) Kinetic energy, which is responsible for heat energy.
- (ii) Potential energy due to the force of attraction between the molecules.

Let K_1 and V_1 be the kinetic and potential energies of the gas on the left side and K_2 , V_2 be the kinetic and potential energies on the right hand side.

Now we shall discuss the behaviour of gases at different temperatures.

For Perfect Gas : For perfect gas Boyle's Law is followed

$$\text{i.e.,} \quad P_1 V_1 = P_2 V_2$$

$$\text{Since} \quad U_1 + P_1 V_1 = U_2 + P_2 V_2$$

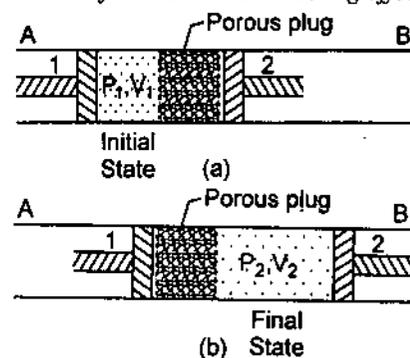


Fig. 9

$$\begin{aligned}
 \therefore U_1 &= U_2 \\
 \text{or } K_1 + V_1 &= K_2 + V_2 \\
 \text{For perfect gas } V_1 &= V_2 \\
 K_1 &= K_2 && (\text{since } K \propto T) \\
 T_1 &= T_2
 \end{aligned}$$

i.e., there is no effect in case of a perfect gas or we can say that the Joule-Thomson effect is zero for a perfect gas.

(a) **Distinction between Joule-Kelvin Expansion and Adiabatic Expansion :** In Joule-Kelvin effect, the gas is forced to pass through the porous-plug, the gas may be cooled, or heated and also may remain unaffected.

In adiabatic expansion, the gas expands suddenly to atmosphere. During the adiabatic expansion, the gas shows cooling effect due to external work.

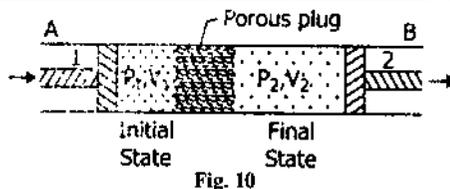
(b) **Joule's Expansion :** Joule expansion is a free expansion in which the gas expands into vacuum without any external work. In this expansion, only internal work is done against intermolecular attraction. In this, the gas always shows cooling effect.

Joule-Thomson Expansion : In Joule-Thomson expansion, the gas is forced to pass through the porous plug under a constant pressure difference. After passing through the porous plug, the gas may be cooled or heated and may also remain unaffected.

• 1.11. EXPRESSION FOR JOULE-THOMSON COOLING

Let us consider a long narrow tube which consists porous-plug E . Two frictionless pistons A and B are fitted in the tube.

Suppose the piston A is moved towards the porous-plug E and a certain mass of the gas is transferred from the left compartment to the right compartment. The compartments are thermally insulated.



Consider a gas of unit mass and let P_1 , V_1 and T_1 be pressure, volume and temperature of the gas before passing through the porous-plug and P_2 , V_2 and T_2 be similar quantities after passing through the porous-plug.

$$\text{Work done on the gas by the piston } A = P_1 V_1$$

$$\text{Work done by the gas on the piston } B = P_2 V_2$$

$$\text{Net work done by the gas} = P_2 V_2 - P_1 V_1$$

van der Waal's equation is given by

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT \quad \dots(1)$$

According to van der Waal, the attractive forces between the molecules of a real gas are due to the internal pressure (a/V^2) of the gas. Hence the internal work done against these forces where 1 gm. molecule expands from V_1 to V_2

$$= \int_{V_1}^{V_2} \frac{a}{V^2} dV = \frac{a}{V_1} - \frac{a}{V_2}$$

Therefore the total work done by the gas

$$W = P_2 V_2 - P_1 V_1 + \frac{a}{V_1} - \frac{a}{V_2} \quad \dots(2)$$

From equation (1),

$$PV + \frac{a}{V} - Pb = RT \quad \left[\text{neglecting } \frac{ab}{V^2} \right]$$

$$\text{or } PV = RT + Pb - \frac{a}{V}$$

$$\text{Thus, } P_1 V_1 = RT_1 + P_1 b - \frac{a}{V_1}$$

and

$$P_2 V_2 = RT_2 + P_2 b - \frac{a}{V_2}$$

Putting these values in equation (2), we get

$$\begin{aligned} W &= RT_2 + P_2 b - \frac{a}{V_2} - RT_1 - P_1 b + \frac{a}{V_1} + \frac{a}{V_1} - \frac{a}{V_2} \\ &= R(T_2 - T_1) - \frac{2a}{V_2} + \frac{2a}{V_1} - b(P_1 - P_2) \end{aligned} \quad \dots(3)$$

Since a and b are very small, therefore from

$$PV = RT$$

or

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

$$\text{Thus, } V_1 = \frac{RT_1}{P_1} \text{ and } V_2 = \frac{RT_2}{P_2}$$

Since T_1 and T_2 differ very little from each other, so

$$dT = T_1 - T_2 \text{ and } T = T_1 = T_2$$

Therefore,

$$W = -RdT + \frac{2a}{RT}(P_1 - P_2) - b(P_1 - P_2)$$

or

$$W = (P_1 - P_2) \left(\frac{2a}{RT} - b \right) - RdT \quad \dots(4)$$

Since the gas is thermally insulated, so the energy necessary for doing this work is drawn from the kinetic energy of the molecules. Hence the kinetic energy decreases and as a result of this there is a fall of temperature by dT .

If C_V is the specific heat of the gas at constant volume, then the heat lost by the gas to do the work W is $C_V dT$.

$$\text{Thus, } C_V dT = (P_1 - P_2) \left(\frac{2a}{RT} - b \right) - RdT$$

or

$$dT(C_V + R) = (P_1 - P_2) \left(\frac{2a}{RT} - b \right)$$

From

$$C_P - C_V = R \text{ or } C_V + R = C_P$$

 \therefore

$$C_P dT = (P_1 - P_2) \left(\frac{2a}{RT} - b \right)$$

or

$$dT = \frac{(P_1 - P_2) \left(\frac{2a}{RT} - b \right)}{C_P} \quad \dots(5)$$

Thus, the cooling at any temperature is directly proportional to the fall in pressure across the porous-plug.

Behaviour of Hydrogen and Helium : Temperature of Inversion

(i) If $2a/RT > b$ then dT is positive, i.e., cooling is produced.(ii) If $\frac{2a}{RT} < b$ then dT is negative, i.e., heating is produced.(iii) If $\frac{2a}{RT} = b$, then dT becomes zero, i.e., no effect.

The temperature at which the gas remains unchanged is called temperature of inversion (T_i) at which Joule-Thomson effect is zero and is given by

$$T_i = \frac{2a}{Rb}$$

The temperature of inversion of hydrogen and helium are much below the room temperature (-80°C and -240°C , respectively) and hence at ordinary temperature, these gases show a heating effect. If these gases are cooled below their temperature of inversion and then pass through the porous-plug, then they will also show a cooling effect.

(b) We have

$$T_i = \frac{2a}{Rb}$$

and critical temperature is

$$T_c = \frac{8a}{27bR}$$

$$\frac{T_i}{T_c} = \frac{2a}{Rb} \times \frac{27bR}{8a} = \frac{27}{4}$$

$$\boxed{\frac{T_i}{T_c} = \frac{27}{4}}$$

Thus, the ratio of the temperature of inversion and critical temperature is independent of the nature of the gas.

(c) Boyle's temperature is

$$T_B = \frac{a}{Rb}$$

and

$$T_i = \frac{2a}{Rb}$$

\therefore

$$\boxed{T_i = 2T_B}$$

This is the relationship between temperature of inversion and Boyle's temperature.

• SUMMARY

- All real gases approach an ideal gas at low pressure.
- The internal energy of an ideal gas is entirely kinetic which depends upon the temperature only and is independent of the volume.
- The rms speed of the molecules of an ideal gas is inversely proportional to the square root of the molecular weight of gas.
- The lighter gas whose molecules have a larger speed, would escape faster than the heavier gas.
- The irregular motion is known as "Brownian motion" of the particle.
- All gases below their temperature of inversion show cooling effect after passing through the porous plug.

• STUDENT ACTIVITY

4. What are the critical constants ?

5. What is Joule-Thomson effect ?

6. Distinguish between Joule-Kelvin expansion and adiabatic expansion.

7. Obtain the ratio between temperature of inversion and critical temperature.

8. Obtain the relation between temperature of inversion and Boyle's temperature.

• TEST YOURSELF

- State the basic assumptions of kinetic theory of an ideal gas. Show that the pressure exerted by an ideal gas is two third of its kinetic energy per unit volume.
- Prove that for a perfect gas whose molecules have n degrees of freedom

$$\frac{C_p}{C_v} = 1 + \frac{2}{n}$$

- Discuss how van der Waal's equation is applicable to real gases.
- What do you understand by Brownian motion? Explain it from kinetic theory.
- Derive van der Waal's equation of state for μ mole of a gas.
- Describe the porous plug experiment and explain the results obtained from it.
- Find an expression for Joule-Thomson cooling produced in a van der Waal's gas.
- The root-mean-square speed for a gas is proportional to :

(a) \sqrt{T} (b) $\sqrt{\frac{1}{T}}$ (c) $\sqrt{2T}$ (d) $\sqrt{\frac{1}{2T}}$

- The critical temperature for a gas is given by :

(a) $T_C = \frac{a}{bR}$ (b) $T_C = \frac{ab}{R}$ (c) $T_C = \frac{8A}{27bR}$ (d) $T_C = \frac{27a}{8bR}$

- Temperature of inversion is given by :

(a) $T_i = \frac{a}{bR}$ (b) $T_i = \frac{2a}{bR}$ (c) $T_i = \frac{ab}{R}$ (d) $T_i = \frac{2ab}{R}$

11. The correct relation between v_{rms} and molecular weight is :

(a) $v_{rms} = \sqrt{\frac{M}{3RT}}$ (b) $v_{rms} = \sqrt{\frac{3RT}{M}}$

(c) $v_{rms} = \sqrt{\frac{3M}{RT}}$ (d) none of these

12. The best example of Brownian motion is :

- (a) N.C.C. parade (b) smoke particles in air
(c) flow of liquid in a tube (d) none of these

13. The ratio of two specific heats of a gas is given by :

(a) $\gamma = 1 + \frac{2}{n}$ (b) $\gamma = 1 + 2n$ (c) $\gamma = 1 + \frac{1}{n}$ (d) none of these

where n is degree of freedom of molecules of a gas.

14. For a triatomic gas, the value of γ becomes :

- (a) 1.33 (b) 1.40 (c) 1.66 (d) none of these

15. The correct equation for a van der Waal's gas is :

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

(c) $\left(p + \frac{a}{V^2}\right)(V - b) = RT$ (d) none of these

where all symbols have their usual meanings.

16. Under Joule-Thomson effect, the change in temperature is given by :

(a) $\Delta T = \frac{\Delta p}{C_V} \left(\frac{2a}{b} - RT\right)$ (b) $\Delta T = \frac{\Delta p}{C_p} \left(\frac{2a}{RT} - b\right)$

(c) $\Delta T = \frac{\Delta p}{C_p} \left(\frac{2ab}{R} - T\right)$ (d) none of these

17. The relation among all critical constants is given by :

(a) $\frac{RV_c}{T_c p_c} = \frac{8}{3}$ (b) $\frac{RT_c}{p_c V_c} = \frac{8}{3}$ (c) $\frac{Rp_c}{T_c V_c} = \frac{8}{3}$ (d) none of these

ANSWERS

8. (a) 9. (c) 10. (b) 11. (b) 12. (b) 13. (a) 14. (a) 15. (c) 16. (b) 17. (b)



LIQUEFICATION OF GASES

STRUCTURE

- Principle of Regenerative Cooling
- Liquefication of Gases
- Principle of Cascade
- Liquefication of Air
- Principle of Liquefying Hydrogen
- Liquefication of Helium
- Approach to Absolute Zero
- Liquid-Helium I and II
 - Student Activity
- Molecules have Finite Diameter
- Mean Free Path
- Transport Phenomena
- Thermal Conductivity on the basis of Kinetic Theory
- Diffusion
 - Student Activity
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Kamerlingh Onne's Cascade System.
- Some important properties of liquid helium-II like extreme fluidity high heat conductivity.
- Formation of films over solid surfaces and the fountain effect.
- Viscosity and its expression and expression of thermal conductivity.

• 2.1. PRINCIPLE OF REGENERATIVE COOLING

The principle of regenerative cooling is based upon the **Joule-Thomson effect**. According to the Joule-Thomson effect when a compressed gas, initially below its temperature of inversion, is forced to pass through a fine nozzle, then its temperature falls. **The fall in temperature is increased as the initial temperature is decreased.** Therefore, the cooled gas emerging from the nozzle is made to flow back over the tube containing the incoming gas. The incoming gas is expanded through the nozzle. Due to this, the gas becomes more cooled. By continuing this process, ultimately a temperature is reached at which the gas is liquefied. This is known as principle of regenerative cooling.

• 2.2. LIQUEFICATION OF GASES

Those substances which are gaseous at ordinary temperature may be converted into liquid state, if they are sufficiently cooled and simultaneously a large pressure is applied to the gas. The phenomenon of liquefication of gases is connected with the production of low temperature.

One general method of liquefying a gas is first to cool it upto its critical temperature and then apply a high pressure upon it. Using this principle Faraday liquefied chlorine and CO₂ by thilorier.

But this principle failed to liquefy those gases which have very low critical temperature. The second method is based upon the fact that the normal boiling point of a substance is always less than its critical temperature. Thus when a gas is cooled below its normal boiling point then it can be liquefied at atmospheric pressure.

Various methods are employed to liquefy gases but the famous experiment of Andrews on carbon-di-oxide (CO_2) performed in 1863 led to the discovery that a gas must be cooled first below its critical temperature and then it can be liquefied by applying pressure. The critical temperature of oxygen, nitrogen, hydrogen and helium are -118°C , -147°C , -240°C and -268°C respectively. With the help of this principle, Pictet in 1877 liquefied oxygen successfully. Pictet cooled O_2 to -30°C , compressed it to 300 atmosphere pressure and then allowed it to expand adiabatically.

Pictet adopted a **cascade process** in which the necessary cooling was obtained step-by-step by evaporation of suitable volatile liquids under reduced pressure. The cascade method failed to liquefy neon, hydrogen and helium. But after the discovery of Joule-Kelvin effect in 1853, it became easy to liquefy gases like hydrogen. It was found that when any gas is compressed to a high pressure and pre-cooled below its temperature of inversion, and passed through a fine nozzle to a region of low pressure, then it is further cooled. At last in 1908 Kamerlingh succeeded in extending the process to liquefy helium, using liquid hydrogen evaporating under reduced pressure as the pre-cooling agent. Thus, all the known gases can be liquefied.

• 2.3. PRINCIPLE OF CASCADE

We know that for the liquefaction of a gas, it is necessary to cool it below its critical temperature. When this temperature is obtained, then gas becomes liquid by applying sufficient pressure. In this process, the lowering of temperature is attained step-by-step with the help of evaporation of suitable volatile liquids. This process is continued until a temperature is attained which is below the critical temperature of the gas to be liquefied. The gas is then liquefied under pressure.

Kamerlingh Onne's Cascade System : The experimental arrangement is shown in fig. (1). It consists of compression pumps P_1 , P_2 and P_3 . A, B and C are the outer jackets filled with cold water, liquid CH_3Cl and liquid C_2H_4 . The pump P_1 compresses CH_3Cl gas and then it is cooled by cold water circulating in the jacket A. When the temperature of CH_3Cl reaches its critical temperature then it becomes liquefied. This liquefied methyl chloride circulates in the jacket B.

The pump P_2 compresses ethylene gas and it is surrounded by the outer jacket B which consists liquid methyl chloride at about -24°C . Liquid methyl chloride is allowed to boil under reduced pressure with the help of the pump P_2 . In this position, the temperature of B reaches to -90°C . The critical temperature of ethylene is 10°C . It is cooled to -90°C and then liquefied by compression.

The liquid ethylene in the jacket C is allowed to boil under reduced pressure with the help of the pump P_2 and finally a temperature of -160°C is attained. The critical temperature for oxygen is -118°C . Oxygen is compressed to a pressure of 25 atmosphere and then it is passed through a spiral tube surrounded by the jacket C. In this position, the liquefied oxygen is obtained and it is collected in a dewar flask.

Advantage : The cascade method is better than other methods. This method is used for liquefying air and oxygen. This method is also used for the continuous production of liquefied gas at a low consumption of energy when proper choice of refrigerants is made.

Disadvantage : The disadvantage of this method is that the liquefaction of every gas cannot be possible, because the lowest temperature obtained by this method is -218°C . Therefore gases like neon and hydrogen whose critical temperature is -229°C and -240°C , cannot be liquefied.

• 2.4. LIQUEFICATION OF AIR

There are two modern processes of the manufacture of air (i) Hampson and Linde process (ii) Claude and Heylandt process. In first process, the cooling is produced by Joule-Thomson effect while in second process, the cooling is produced both by Joule-Thomson effect and adiabatic expansion of air.

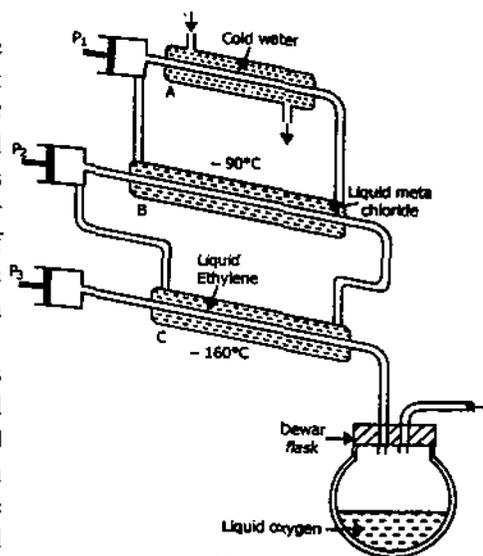


Fig. 1

Linde's Process : The experimental arrangement is shown in fig. (2). It consists of stage compressors P_1 and P_2 which are used to compress air from 1 to 20 and 20 to 200 atmosphere. Air

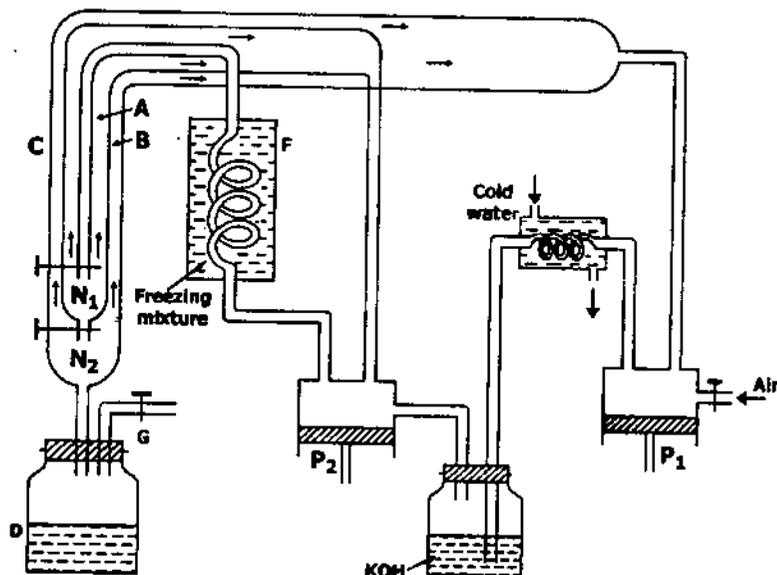


Fig. 2

which is compressed to 20 atmosphere pressure by the compressor P_1 is first allowed to pass to a cooled water bath to remove the heat of compression and secondly to flow through KOH, CaCl_2 and P_2O_5 to remove CO_2 and water vapours. If CO_2 and water vapours are present then they will solidify the air and hence liquefied air can not be obtained and circulation of the system is blocked.

Now the air is compressed 200 by atmosphere pressure by the compressor P_2 and then passed through the spiral tube which is cooled to -20°C by a freezing mixture. Now it is cooled at high pressure and passed through the liquefying section and enters through the tube A to the nozzle N_1 where it suffers a drop in pressure. In this position, when the gas expands to 20 atmospheres pressure, then the temperature falls to about -70°C . If the nozzle N_2 is closed then the cooled air passes through a wide tube B enclosing A and returns to the compressor P_2 . Due to this, the incoming gas is cooled in the tube A. This process is continued and after some cycles the air is cooled to a very low temperature -183°C and hence the liquefied air is obtained. At this stage, the second nozzle N_2 is opened. The air is allowed to expand to one atmosphere pressure where it becomes liquefied. The unliquefied air is fed back through the tube C surrounding B to the compressor P_1 .

Use of Liquid Air : The liquid air is used to cool the substances to very low temperature and on creating high vacuum by solidifying a gas less volatile than air. It is also used for the separation and purification of gases.

• 2.5. PRINCIPLE OF LIQUEFYING HYDROGEN

The critical temperature of hydrogen is -240°C which is very low. Cascades failed to liquefy hydrogen because a gas above its critical temperature can not be liquefied. Olszewski succeeded in producing traces of liquid hydrogen in 1895. But this method did not solve the problem. The problem was solved by Joule-Thomson method. According to Joule-Thomson effect, any compressed gas below its temperature of inversion is cooled when expanded through a nozzle.

Since the temperature of inversion for hydrogen is -80°C , therefore hydrogen should be pre-cooled below this temperature but it is found that this pre-cooling is not enough for its liquefaction. The Boyle temperature of hydrogen is -177°C . This means that hydrogen should be pre-cooled upto this temperature. By Joule-Thomson process Dewar liquefied the hydrogen.

Liquefaction of Hydrogen : The experimental arrangement of hydrogen liquefier is shown in the fig (3). For complete insulation, the whole apparatus is enclosed in an outer Dewar flask L.

Hydrogen is passed through a coil at pressure of 200 atmosphere. The coil is immersed in solid CO_2 and alcohol. It passes through the coil in the chamber A where it is further cooled. The chamber B contains liquid air which cools hydrogen in the coil E. The liquid air is allowed to boil under reduced pressure in the chamber C and in coil F is cooled to -200°C . When this cooled hydrogen passes through the regenerative coil G then under Joule-Thomson effect, liquefied hydrogen is obtained.

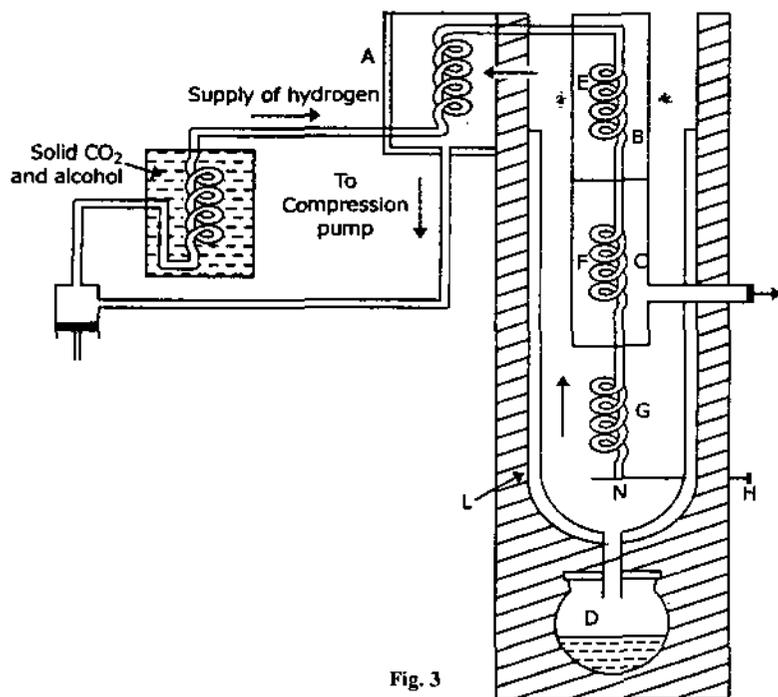


Fig. 3

• 2.6. LIQUEFICATION OF HELIUM

Helium could not be liquefied for a long time. The reason was that, the critical temperature of helium is -268°C which is very low. In 1908, Kamerlingh Onnes liquefied it. Hence it is necessary to cool it below -268°C . By the method of cascade, the lowest temperature using liquid oxygen evaporating under reduced pressure is -218°C . Hence the method is not applicable to liquefy helium.

In 1908, K. Onnes found that the temperature of inversion for helium is -240°C and it is possible to cool it below this temperature with the help of liquid hydrogen evaporating under reduced pressure. He liquefied helium by pre-cooling it to a temperature of -256°C by using a bath of liquid hydrogen boiling under reduced pressure.

The gas then suffers Joule-Thomson expansion and becomes liquefied.

Kapitza's Helium Liquefier : Kapitza in 1934 liquefied helium with the help of Claude's method. This method is based on the combined action of adiabatic expansion and Joule-Thomson effect. The structural diagram of this method is shown in the fig. (4).

Pure and dry helium under a pressure of 30 atmosphere is pre-cooled to -208°C by passing it through a bath of liquid nitrogen boiling under reduced pressure. Now the compressed cooled gas

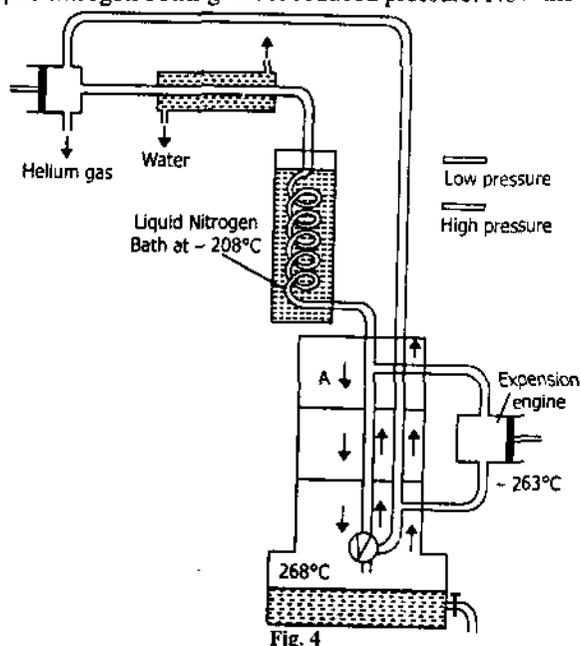


Fig. 4

is divided into two parts at A. A part of this pre-cooled helium is directed towards expansion engines where it is cooled to a temperature of -263°C . A small gap is left between the cylinder and the piston of the expansion engine. This means that the piston is loosely fitted in the cylinder. When the compressed gas is passed through the engine, then a part of it escapes through this clearance which works as a lubricant. At the same time expansion is so rapid that the escaped part is inappreciable. This part cools the second part coming towards the expansion valve in the heat exchanger. Second part is so cooled that after the expansion, it is liquefied.

• 2.7. APPROACH TO ABSOLUTE ZERO

When helium under reduced pressure is boiled, then its temperature reaches to less than 1K. K. Onnes attained a temperature of 0.82K by evaporating liquid helium under a pressure of 0.013 mm. of mercury. In this manner, the temperature becomes 0.726K which was obtained by Keesom who reduced the pressure on the surface of liquid helium down to 0.0036 m.m. of mercury by extremely powerful pumps.

Principle : The adiabatic demagnetisation method, which is used to obtain very low temperature, was given by Debye and Giauque in 1926. It is based upon the principle of **magnetic caloric effect**. In paramagnetic substances the molecules are distributed in random manner. When this substance is placed in magnetic field then the molecules set themselves in the direction of magnetic field. For this, some external work is required. This work is added to the internal energy of the substance and hence its temperature rises. When a substance which is already magnetised, is suddenly demagnetised then it shows cooling effect.

Method : The experimental arrangement is shown in the fig. (6). The paramagnetic substance is suspended in a vessel, which is surrounded by the liquid helium. The liquid helium is boiled under reduced pressure. It is surrounded by a flask containing liquid hydrogen. The substance remains in contact with helium gas.

When a strong magnetic field of 30,000 gauss is applied, then the temperature of the paramagnetic substance increases. But the heat is conducted by helium gas rapidly and the temperature of the salt falls to the original temperature of the helium bath. The helium gas is pumped out and the salt is thermally isolated.

When the magnetic field is removed then the temperature of the paramagnetic substance falls due to the adiabatic demagnetisation. The temperature of the paramagnetic substance can be obtained by the following formula

$$\chi = \frac{C}{T}$$

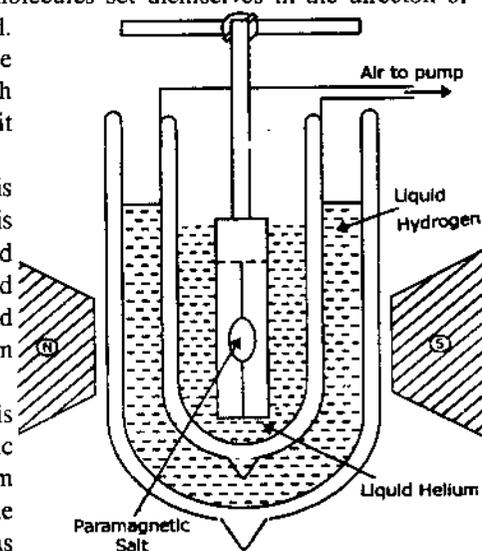
where χ is the magnetic susceptibility and C is the constant. Hence, if the susceptibility be measured then the corresponding temperature can be obtained.

• 2.8. LIQUID-HELIUM I AND II

Helium gas liquefies at 1 atmosphere pressure and 4.2 K. When the temperature of liquid helium is lowered then a new phenomenon is obtained. When the temperature falls from 4.2K to 2.19K, then the boiling stops and the liquid becomes quiet. This means that below 2.19K, a new liquid phase of helium is formed. This is called liquid helium II and the temperature 2.19K is called λ -point. The liquid helium above λ -point is known as liquid helium I. Hence, liquid helium I changes to liquid helium II at 2.19K.

Properties of Liquid Helium II : Some important properties of liquid helium II are as follows:

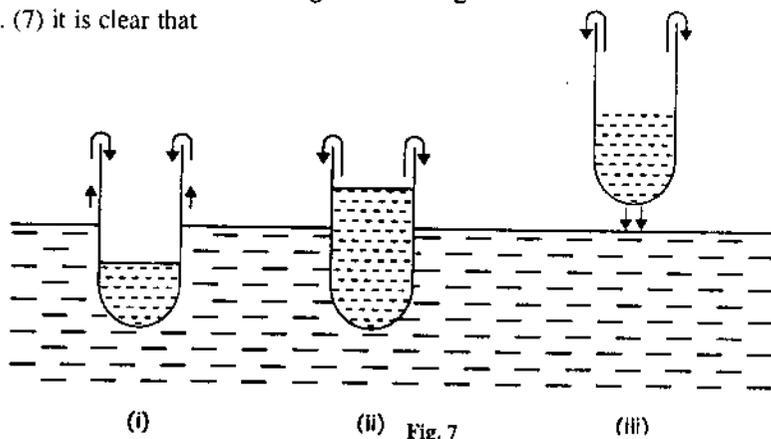
(i) **Extreme Fluidity :** The viscosity of liquid helium II is less than that of hydrogen gas. It has approximately zero viscosity and can flow rapidly without resistance through narrow tubes. Due to this reason it is called a **super fluid**. Kapitza found that



$$\frac{\text{viscosity for liquid He II}}{\text{viscosity for liquid He I}} = 10^{-3}$$

(ii) **High Heat Conductivity** : Coefficient of thermal conductivity is very high. It is said to possess about 13.6×10^6 times more conductivity than liquid helium I.

(iii) **Formation of Films Over Solid Surfaces** : Liquid helium II forms a thin film on solid surfaces. This film is known as rolling film. Through this film it flows from one vessel to another from fig. (7) it is clear that

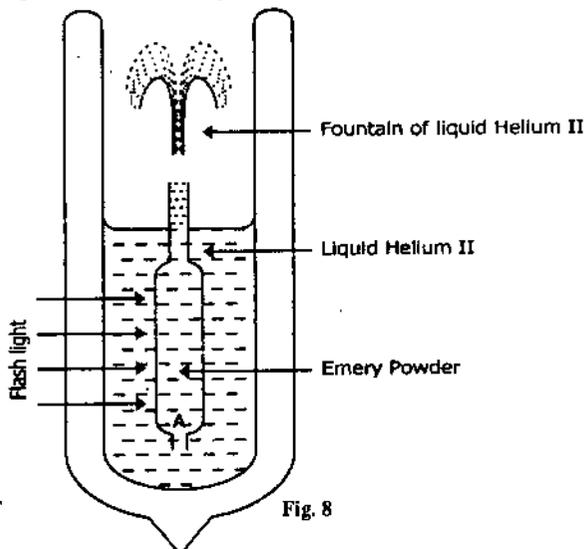


- (a) It can creep into vessel when the vessel is lowered into the liquid.
- (b) When the vessel containing helium II is taken out of the liquid, then it creeps out of the vessel and continues to flow until the two levels (outside and inside) are the same.
- (c) When the vessel is completely out of the liquid, then helium II creeps and flows down the outer surface of the vessel. It continues to flow until the vessel is empty.

(iv) **Heat of Vaporisation and Surface Tension** : Liquid helium II has high heat of vaporisation and small surface tension. It has large specific heat at 2.19K. It is due to the rapid decrease of its entropy with decreasing temperature. This is a complicated phenomenon and statistical mechanics cannot be applied while Bose-Einstein statistics can be applied.

(v) **The Fountain Effect** : Another phenomenon of liquid helium II is the "fountain effect" given by Allen and Jones in 1938. Helium II is taken in a tube which is open at both ends and kept inside a Dewar flask also containing liquid helium II.

The upper part of the tube is in the form of a capillary and is kept projecting out of the liquid helium of the flask. The lower part of the tube is packed with fine emery powder. The separation between the powder particles provides fine capillaries for liquid helium II to flow into the tube. When heat radiations are incident on this powder, then liquid helium is found to spurt out of the capillary tube in the form of a fountain as shown in the fig. (8). This is called fountain effect.



• **STUDENT ACTIVITY**

1. What is the principle of regenerative cooling ?

2. What is principle of cascade ?

3. What are the uses of liquid air ?

• 2.9. MOLECULES HAVE FINITE DIAMETER

According to kinetic theory of gases, the molecules of a gas move with very high velocity at ordinary temperature. This means that with such high velocity the molecules of gas filled in a vessel should disappear in no time, but in practice it is not so and we find that a cloud of smoke holds together for hours, *i.e.*, it does not disappear at once. Therefore, Clausius pointed out that we should not consider the molecules as geometrical point, but they have certain dimensions and hence molecules are particles having finite size. Therefore molecules of gas collide with each other due to their finite size.

• 2.10. MEAN FREE PATH

The molecules of a gas in a vessel move with very high speed, due to this they collide with each other elastically. Since the molecules do not exert any force on each other except at collision, therefore they move in straight line paths with constant speed between two successive collisions. It is found that the path of a single molecule is a series of short zig-zag paths of different lengths. These paths are known as 'free paths' and their mean is known as 'mean free path'.

Expression for Mean Free Path : Now we have to calculate the expression for mean free path. For this, let all the molecules of a gas except one be at rest. Let d be the diameter of a molecule. This molecule will collide with all those molecules whose centres are at a distance d from its centre as shown in fig. (10).

Collision will also occur if the colliding molecule has a diameter $2d$ and all the other molecules are point particles as shown in fig. (10). Let us consider a molecule of diameter $2d$, moving with velocity v through a gas of equivalent point particles. Let the molecule and point particles exert no force on each other. In time t the moving molecule will sweep out a cylinder of length vt and cross-sectional area πd^2 as shown in fig. (11). In time t this molecule will collide with every other molecule whose centre lies in this cylinder. Thus if

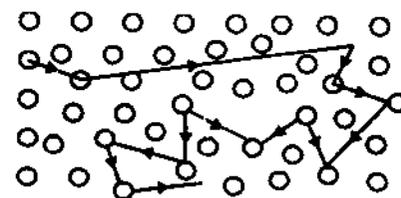


Fig. 9

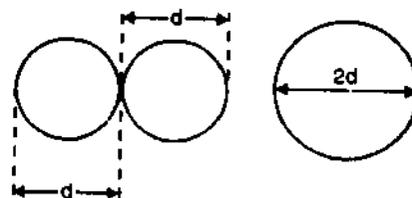


Fig. 10

there are n molecules per unit volume, then the number of collisions made in time t by the molecule is

$$= n \times \text{volume of the cylinder}$$

$$= n \times \pi d^2 vt$$

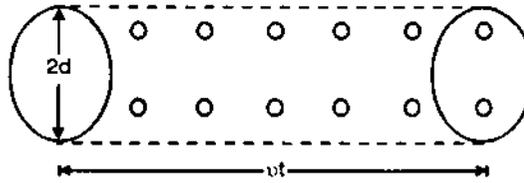


Fig. 11

Since the mean free path is the average distance between the collisions

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

If all other molecules are at rest, then the mean free path will be

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

This is the required expression for the mean free path. From this expression it is clear that the mean free path is inversely proportional to the number of molecules per unit volume, *i.e.*, density. Thus, **the mean free path varies inversely as the density of the gas.**

Variation with Pressure and Temperature :

From $PV = NkT$

$$P = \left(\frac{N}{V}\right)kT$$

or $P = nkT$

where N is the total number of molecules and n is the total number of molecules per unit volume

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

Putting in equation (1)

$$\lambda = \frac{kT}{\sqrt{2} \pi p d^2}$$

or $\lambda \propto \frac{1}{p}$ and $\lambda \propto T$

i.e., mean free path is inversely proportional to pressure (p) and directly proportional to the temperature (T) of the gas.

2.11. TRANSPORT PHENOMENA

According to kinetic theory of gases, the molecules are moving in all possible directions with different speeds. *i.e.*, there is a relative motion of the gas layers and hence this gives rise to the phenomenon of **viscosity**. The temperature of the molecules may not be the same and hence heat flows from higher to lower temperature. This gives rise to the phenomenon of **conduction**.

The number of molecules per unit volume (n) may not be the same throughout the volume of the gas and hence molecules wave from higher value of (n) to lower value of n . This gives rise to the phenomenon of **diffusion**.

Thus, the transport of momentum, energy and mass represent viscosity, conduction and diffusion, respectively.

These are called "transport phenomena".

These transport phenomena are irreversible and occur only in the non-equilibrium state of the gas.

Viscosity : Here we shall discuss the phenomenon of viscosity based on the mean free path. Consider a gas in motion in XY plane such that there is a mass motion of the gas parallel to XY plane but no mass motion along the Z -axis. Consider an imaginary plane AB . The layers of the gas above AB are moving with a greater mass velocity* in the direction of arrow as shown in (Fig. 12), while those below are moving with a smaller mass velocity in the same direction.

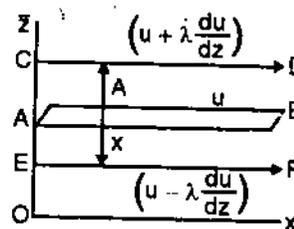


Fig. 12

*Mass velocity means the velocity of mass of the gas as a whole and not velocity of individual molecule.

The tendency of the layer above AB is to accelerate the motion of the layer below AB , while the tendency of the layer below AB is to retard the motion of the layer above AB . Due to this fact, there is a difference in velocity on the two sides of AB . This property of the gas is known as its viscosity. The fundamental law of viscosity is that the magnitude of the viscous force f is proportional to the area A and the velocity gradient $\frac{dv}{dz}$ i.e.,

$$f \propto \frac{dv}{dz} \text{ or } f = \eta \frac{dv}{dz}$$

or
$$\frac{f}{A} = \eta \frac{dv}{dz}$$

But
$$\frac{f}{A} = F$$

so that
$$F = \eta \frac{dv}{dz}$$

or
$$* \quad \eta = \frac{F}{dv/dz}$$

where η is the coefficient of viscosity.

Explanation on the Basis of Kinetic Theory :

The molecules above the plane AB having greater mass velocity possess greater momentum in a horizontal direction than those below it. Of course, there is no mass motion in the z direction due to the advancement of the gas but some of these molecules will be moving downwards across the plane AB due to the thermal agitation. Similarly, some molecules having small momentum from the lower side of AB are also moving in the upward direction. In this way, the slower stream of gas below AB gains momentum while the faster stream above AB loses momentum. But according to the Newton's law of motion, the loss in momentum means a force in the backward direction, and the gain in momentum means a force in forward direction. Thus the layer above AB experiences a force in backward direction.

Expression for Viscosity : Now the molecules which move towards the surface AB are only those which on the average lie within the mean free path λ . Let u be the mass velocity of the gas along the plane AB , and $\frac{du}{dz}$ the velocity gradient in the upward direction perpendicular to AB . Then

the mass velocity of the gas along CD and EF will be $\left(u + \lambda \frac{du}{dz}\right)$ and $\left(u - \lambda \frac{du}{dz}\right)$ respectively.

Let n be the number of molecules per c.c and \bar{v} their average velocity due to thermal agitation with which they are moving constantly in all possible directions. Then the number of molecules* crossing unit area of AB downwards in one second is $\frac{n\bar{v}}{6}$ and an equal number crossing upwards.

Taking m to be the mass of a molecule, the total mass crossing unit area of AB per second either side = $\frac{1}{6} m n \bar{v}$.

The momentum carried downwards by the molecules crossing unit area of AB per second from the plane CD is, therefore

$$\begin{aligned} &= \text{mass} \times \text{velocity} \\ &= \frac{1}{6} m n \bar{v} \times \left(u + \lambda \frac{du}{dz}\right) \end{aligned}$$

Similarly, the momentum carried upwards

$$= \frac{1}{6} m n \bar{v} \times \left(u - \lambda \frac{du}{dz}\right)$$

Net momentum transferred per second downwards.

$$\begin{aligned} &= \frac{1}{6} m n (\bar{v}) \left(u + \lambda \frac{du}{dz}\right) - \frac{1}{6} m n \bar{v} \left(u - \lambda \frac{du}{dz}\right) \\ &= \frac{1}{3} m n \bar{v} \lambda \frac{du}{dz} \end{aligned}$$

But this net transfer of momentum per second must be equal to $\eta \frac{du}{dz}$ as already explained.

Hence

$$\begin{aligned}\eta \frac{du}{dz} &= \frac{1}{3} m n \bar{v} \lambda \frac{du}{dz} \\ \eta &= \frac{1}{3} m n \bar{v} \lambda \\ &= \frac{1}{3} \rho \bar{v} \lambda \quad \dots(1)\end{aligned}$$

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

We also know that

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

then

$$\begin{aligned}\eta &= \frac{1}{3} m n \bar{v} \lambda = \frac{1}{3} m n \bar{v} \times \frac{1}{\sqrt{2} \pi n d^2} = \frac{1}{3\sqrt{2}} \cdot \frac{m \bar{v}}{\pi d^2} \\ \eta &= \frac{1}{3\sqrt{2}} \frac{m \bar{v}}{\pi d^2} \quad \dots(2)\end{aligned}$$

where d is the molecular diameter. This expression is independent of n , hence shows that for a given temperature (\bar{v} constant), the coefficient of viscosity is independent of pressure.

• 2.12. THERMAL CONDUCTIVITY ON THE BASIS OF KINETIC THEORY

The thermal conductivity of gases can be explained in the same way as in the case of viscosity of gases. The only difference is that here the molecules are considered as carriers of heat energy instead of momentum. Let us suppose that the mass of the gas is at rest and CD and EF represent the hot and cold layers of the gas as shown in fig. 13.

The molecules coming from the higher temperature side CD and passing downward the plane AB possess a greater kinetic energy than those coming from low temperature side and passing through AB on the upward side. Hence the average kinetic energy of the molecules below AB is continuously increasing while that above AB is decreasing. In this way we can say that the temperature below AB is increasing while above AB is falling. That is, the conduction is due to the transport of energy.

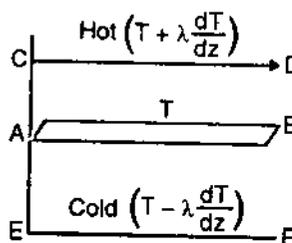


Fig. 13

Expression for Thermal Conductivity

Consider a layer AB of the gas at a temperature T and let the temperature gradient be dT/dz . Now the molecules which move towards the surface AB are only those which on the average lie within the mean free path λ . Hence the temperature of CD and EF layers would be respectively.

$$\left[T + \lambda \frac{dT}{dz} \right] \text{ and } \left[T - \lambda \frac{dT}{dz} \right]$$

Let n be the number of molecules per c.c. and \bar{v} their average velocity due to thermal agitation with which they are moving constantly in all possible directions. Then the number of molecules crossing unit area of AB downwards in one second is $n\bar{v}/6$ and an equal number crossing upwards. Taking m to be the mass of molecule, the total mass crossing unit area of AB per second either side is $\frac{1}{6} m n \bar{v}$.

Hence total heat carried by all the molecules moving downwards and crossing the layer AB per unit area per second

$$\begin{aligned}&= \text{mass} \times \text{specific heat} \times \text{temperature} \\ &= \frac{mn \bar{v}}{6} \times C_v \times \left[T + \frac{dT}{dz} \lambda \right]\end{aligned}$$

Similarly total heat carried by all molecules moving upward and crossing AB per unit area per second

$$= \frac{mn \bar{v}}{6} \times C_v \times \left[T - \frac{dT}{dz} \lambda \right]$$

*We can regard that n molecules are moving along the three vertical axes in upward and downward directions, hence one sixth are moving in the downward direction.

Hence net transfer of heat per unit area per second

$$\begin{aligned} Q &= \frac{mn\bar{v}}{6} C_v \left[T + \frac{dT}{dz} \lambda \right] - \frac{mn\bar{v}}{6} C_v \left[T - \frac{dT}{dz} \lambda \right] \\ &= \frac{mn\bar{v}}{6} C_v \cdot \frac{2dT}{dz} \lambda \\ &= \frac{1}{3} mn\bar{v} \lambda \frac{dT}{dz} C_v \end{aligned}$$

The coefficient of thermal conductivity K of a gas is defined as the quantity of heat that flows per unit area, per unit time, per unit temperature gradient and is given by

$$Q = K \frac{dT}{dz}$$

or

$$\begin{aligned} K &= \frac{Q}{dT/dz} \\ &= \frac{\frac{1}{3} mn\bar{v} \lambda \frac{dT}{dz} C_v}{\frac{dT}{dz}} \\ &= \frac{1}{3} mn \bar{v} \lambda C_v \end{aligned} \quad \dots(1)$$

We also know that

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

so that

$$\begin{aligned} K &= \frac{1}{6} mn \bar{v} \frac{1}{\sqrt{2} \pi n d^2} C_v \\ &= \frac{1}{3 \sqrt{2}} \cdot \frac{m \bar{v} C_v}{\pi d^2} \end{aligned} \quad \dots(2)$$

which is the required expression for coefficient of thermal conductivity of a gas.

• 2.13. DIFFUSION

Let us consider that a mass of the gas moving between parallel planes AB and CD . Suppose the concentration (number of molecules per c.c.) increases in vertical direction as we go from AB to CD through the intermediate plane XY . Therefore concentration of gas above XY is greater than that below XY . Thus in order to bring the equilibrium, the molecules of the gas will cross the plane XY from AB to CD and *vice-versa*, due to thermal agitation. This diffusion of gas molecules through the intermediate plane can be considered as the transport of mass.



Fig. 14

Let n = co-ordination at the plane XY

$\frac{dn}{dz}$ = rate of change of concentration in vertical direction, called concentration gradient.

Then concentration at plane CD is

$$= n + \lambda \frac{dn}{dz}$$

where λ is the distance between plane CD and XY or plane AB and XY (XY is in middle). This is equal to mean free path.

$$\text{Concentration at plane } AB = n - \lambda \frac{dn}{dz}$$

As molecules are moving in all possible directions due to thermal agitation, we can take that $1/3$ of the total number move along any axis of $1/6$ of molecules along any axis in *one particular* direction. Then number of molecules crossing plane XY downwards per unit area per second will be

$$= \frac{1}{6} \bar{v} \left(n + \lambda \frac{dn}{dz} \right)$$

and those upward will be

$$= \frac{1}{6} \bar{v} \left(n - \lambda \frac{dn}{dz} \right)$$

so that net number crossing unit area per second of plane XY in downward direction is

$$\begin{aligned} &= \frac{1}{6} \bar{v} \left(n + \lambda \frac{dn}{dz} \right) - \frac{1}{6} \bar{v} \left(n - \lambda \frac{dn}{dz} \right) \\ &= \frac{1}{3} \bar{v} \lambda \frac{dn}{dz} \end{aligned}$$

Coefficients of diffusion,

$$\begin{aligned} D &= \frac{\text{No. of molecules across unit area per sec.}}{\text{concentration gradient}} \\ &= \frac{1}{3} \bar{v} \lambda \frac{dn}{dz} \\ &= \frac{1}{3} \bar{v} \quad \dots(1) \\ &= \frac{1}{3} \frac{\rho \bar{v} \lambda}{\rho} = \frac{\eta}{\rho} \quad \dots(2) \end{aligned}$$

where $\eta = \frac{1}{3} \rho \bar{v} \lambda$ and is called coefficient of viscosity. Also

$$\lambda \propto \frac{1}{n} \propto \frac{T}{p} \quad \text{and} \quad \bar{v} \propto \sqrt{T}$$

so that

$$D \propto \frac{T^{3/2}}{p}$$

that is coefficient of diffusion is directly proportional to $T^{3/2}$ (absolute temperature) and is inversely proportional to pressure p .

• SUMMARY

- All the known gases can be liquefied.
- The liquid air is used to cool the substances to very low temperature and on creating high vacuum.
- The adiabatic demagnetisation method is used to obtain very low temperature.
- Helium gas liquefies at 1 atmosphere pressure and 4.2 K.

• STUDENT ACTIVITY

4. Show that molecules have finite diameter.

5. What is mean free path ?

• TEST YOURSELF

1. Write short note on the liquification of gases.
2. Describe the method used in the manufacture of liquid air.
3. Describe a method of liquifying hydrogen.
4. Explain the method of liquifying the helium gas.
5. Explain the principle of adiabatic demagnetisation and the method for reaching temperature near absolute zero.
6. Give some important properties of liquid helium II.
7. What do you understand by mean free path of the molecules of a gas? Obtain an expression for it.
8. What are the transport phenomenon in gases. Explain viscosity of gases on the basis of kinetic theory of gases. Derive an expression for the coefficient of viscosity.
9. Explain conduction on the basis of kinetic theory of gases. Show that the coefficient of conductivity of a gas is independent of its pressure.
10. Can we consider the phenomenon of diffusion as the transport of mass? Obtain an expression for the coefficient of diffusion.
11. According to kinetic theory of gases, the molecules of a gas move in :
 - (a) only one fixed direction
 - (b) all possible directions
 - (c) along three axis
 - (d) none of these
12. Mean free path of a molecule depends upon :
 - (a) square of the diameter of the molecule
 - (b) the number of molecules per unit volume
 - (c) both of (a) and (b)
 - (d) none of the above
13. The mean free path of a molecule depends upon :
 - (a) absolute temperature of the gas
 - (b) pressure of the gas
 - (c) volume of the gas
 - (d) (a) and (b) only
14. Transportation of any quantity in a gas occurs only when :
 - (a) gas is in equilibrium
 - (b) gas is in inequilibrium
 - (c) gas is in any state
 - (d) none of these
15. If cooling of a gas is obtained step by step by evaporation of suitable volatile liquid under reduced pressure, then this process is known as :
 - (a) Cascade process
 - (b) Adiabatic process
 - (c) Regenerative cooling
 - (d) None of these
16. The ratio of temperature of inversion and critical temperature is a constant and is equal to :
 - (a) $27/2$
 - (b) $27/4$
 - (c) $27/8$
 - (d) 27×2
17. Liquefaction of hydrogen is obtained with the help of :
 - (a) Joule-Kelvin effect
 - (b) Isothermal effect
 - (c) Adiabatic expansion
 - (d) none of these
18. Liquefaction of helium is obtained with the help of :
 - (a) Joule-Kelvin effect
 - (b) Adiabatic expansion
 - (c) Combination of (a) and (b)
 - (d) none of these

ANSWERS

11. (b) 12. (c) 13. (d) 14. (b) 15. (a) 16. (b) 17. (a) 18. (c)



UNIT

3

THERMODYNAMICS

STRUCTURE

- Thermodynamic System
- Internal Energy of a System
- Cycle
 - Student Activity
- Reversible and Irreversible Processes
 - Student Activity
- Heat Engine
- Carnot's Heat Engine (Reversible heat engine)
- Carnot Ideal Refrigerator
- Carnot's Theorem
- Absolute Scale of Temperature
- Entropy
- Temperature-Entropy ($T-S$) Diagram
- Principle of Increase of Entropy
- Entropy of a Perfect Gas
- Entropy of a System
- Relation between Entropy and Maximum Probability
 - Summary
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Zeroth law of thermodynamics
- First law of thermodynamics.
- Cyclic process, isobaric process, isochoric process, adiabatic process and free expansion.
- Condition of reversibility
- Efficiency of heat and indicator diagram.
- Absolute zero.
- Change of entropy in reversible and irreversible processes.
- Entropy change of universe due to reversible and irreversible processes; Principle of degradation of energy.

• 3.1. THERMODYNAMIC SYSTEM

A thermodynamic system is that which can be described in terms of the thermodynamic co-ordinates, pressure (P), volume (V), temperature (T) and entropy (S). Examples of thermodynamic system are :

1. Stretched wire : In a stretched wire, to find Young's modulus of wire by stretching the complete thermodynamic co-ordinates are :

(i) F (ii) L (iii) T

$$Y = \frac{F \cdot L}{\Delta L \cdot A}$$

The pressure and volume are considered to be constant.

(ii) **In cells** : The thermodynamic co-ordinates to describe completely the cell are :

(i) The E.M.F. of the cell (ii) the change that flows (iii) the temperature.

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 co-ordinates (P , V , T and S) remain constant until the external condition does not change.

Temperature : Temperature can be defined as **the property that determines whether the body is cold or hot**. It may also be defined as **“that physical quantity which gives the direction of the flow of heat is known as temperature.”** If two systems are in thermal equilibrium, they will have same temperature.

Heat : Heat is a form of energy which produces in us the sensation of warmth. Heat is the form of energy, due to the kinetic energy of the molecules constituting the body.

Zeroth Law of Thermodynamics : According to this law, **“if A and B are in thermal equilibrium with a third body C, then A and B are in thermal equilibrium with each other”**. But it is not always true. For example, if Sunil and Anil are friends of Devesh, then it is not necessary that Sunil and Anil are also friends.

Zeroth law of thermodynamics can be related with temperature. It leads to the fact that all systems in thermal equilibrium with one another have a common property. This property is known as “temperature”.

• 3.2. INTERNAL ENERGY OF A SYSTEM

Each gas is made of very small particles, called molecules. These molecules are in random motion and due to this they possess energy, known as kinetic energy. They exert the force of attraction on each other, due to this they possess the energy, which is known as potential energy. The sum of these two energies ($K.E. + P.E.$) is known as internal energy of the gas. The molecules of an ideal gas do not possess potential energy (because they do not exert the force of attraction on each other), and hence the internal energy of an ideal gas is only the kinetic energy of its molecules.

First Law of Thermodynamics : This law states only about the conservation of energy and this law gives the relationship between the work and heat produced. According to this law **“whole of the work done is used in producing heat or vice-versa, i.e.,**

$$W = JQ$$

where J is known as mechanical equivalent of heat.

But in practice it does not do so. When a certain amount of heat is supplied to a system, the whole of the heat energy may not be converted into work. A part of the heat may be used in doing external work and rest of the heat may be used in increasing the internal energy of the molecules. i.e.,

$$dQ = dU + dW$$

This is the differential form of first law of thermodynamics, i.e., the first law of thermodynamics states that the amount of heat given to a system is equal to the sum of the increase in internal energy of the system and the external work done.

Significance : This law gives the exact relation between heat and work. From this law it is clear that, it is impossible to get the work from any machine without giving some amount of energy in any form to surroundings.

• 3.3. CYCLE

When a system goes from initial state to final state, through different processes and then comes back to its initial state, then the system is said to have undergone a ‘cycle’.

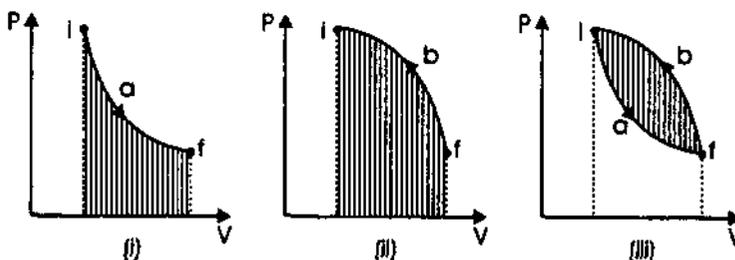


Fig. 1. The three figures show (i) expansion, (ii) compression and (iii) a cycle

Consider a system which goes from initial state i to the final state f through the path a and then comes back to its initial state i through the path b as shown in the fig. [1(iii)]. During the path a , the system expands. In this position the work is done by the system. This work is equal to the area $iafcd$.

During the path b , the system is compressed and work is done on the system. This work is equal to the area $ibfcd$.

The net work done by the system, is equal to the shaded area.

If the work is done by the system, then it is said to be positive work and if the work is done on the system then, it is said to be negative work.

(a) **A Cyclic Process** : The process during which the change in the internal energy is zero is called cyclic process. That is, for cyclic process, we have

$$dU = 0$$

From first law of thermodynamics

$$dU = Q - W$$

$$\therefore 0 = Q - W$$

$$\text{or } \boxed{Q = W}$$

In the differential form, we have $\oint dQ = \oint dW$

Thus, for closed system during cyclic process, the cyclic integral of heat is equal to the cyclic integral of work.

(b) **Isobaric Process** : The process during which pressure remains constant is known as isobaric process. The boiling of water to steam and freezing of water to ice are the examples of isobaric processes, because during these processes, the pressure and temperature remain constant.

Consider the phase change of mass m of the liquid to vapour at constant temperature and pressure. Let V_1 and V_2 are the volumes of liquid and vapour, respectively.

Work done in expanding from volume V_1 to V_2 is

$$W = P(V_2 - V_1)$$

If L is the latent heat, then heat absorbed by the mass m during the phase change is

$$Q = mL$$

From first law of thermodynamics

$$\Delta U = Q - W$$

$$\Delta U = mL - P(V_2 - V_1)$$

(c) **Isochoric Process** : The process during which volume remains constant is known as isochoric process. In such a process, the work done on or by the system is zero because change in volume is zero.

From first law of thermodynamics

$$\Delta U = Q - W$$

$$= Q - P\Delta V$$

$$= Q - 0$$

$$[\Delta V = 0]$$

$$= Q$$

$$\therefore \boxed{\Delta U = Q}$$

From this, it is clear that the heat added to the system or heat taken from the system is entirely used to increase or decrease the internal energy of the system, respectively.

(d) **Adiabatic Process** : During adiabatic process no heat flows into or out of the system, i.e.,

$$Q = 0$$

From first law of thermodynamics

$$\Delta U = Q - W$$

$$\Delta U = 0 - W$$

$$[\because Q = 0]$$

$$\Delta U = -W$$

Thus, during an adiabatic process the work done is exactly equal to the change in the internal energy of the system. During this process if the work is done by the system, then its internal energy decreases and hence its temperature decreases and if the work is done on the system, then its internal energy increases and hence its temperature will increase.

(e) **Free Expansion** : If a system expands in such a way that no heat enters or leaves the system and also no work is done by or on the system, then the expansion is known as "free expansion". Thus, free expansion is an adiabatic process in which no work is done on or by the system.

From first law of thermodynamics,

$$\Delta U = Q - W$$

Here $Q = 0$ and $W = 0$

Therefore, $\Delta U = 0$

Thus, the change in internal energy is zero for free expansion.

• **STUDENT ACTIVITY**

1. Define first law of thermodynamics.

2. State the physical significance of first law of thermodynamics.

• **3.4. REVERSIBLE AND IRREVERSIBLE PROCESSES**

The reversible process is one in which the working substance passes exactly through the same stages as in the direct process but the internal and mechanical effects at each stage are exactly reversed. **For example, if certain amount of work is obtained by supplying a certain quantity of heat in direct process then the same amount of heat should be obtained by performing the same amount of work in the reverse direction. If it is not so then the process is known as irreversible.**

Condition of Reversibility :

(i) Dissipative forces like friction, viscosity, electrical resistance must be absent. If the piston is not frictionless then during compression, the work will also be done against the frictional forces. Thus, when the piston moves in forward or backward direction the work against the frictional forces will always be done. This means that the work done against frictional forces can not be recovered by reversing the process and hence for reversible process friction should not be present.

(ii) Process must take place infinitely slowly, i.e., quasi-static. During compression, some work is converted into kinetic energy of the piston and in the form of eddies in the gas. This work is not removed during the reversible process. If the motion of the piston is infinitely slow, then the pressure of the gas on the piston should be only infinitesimally different from the pressure exerted by the piston on the gas.

(iii) The temperature of the system must not differ appreciably from its surroundings. If there is an infinitesimal temperature difference, then the heat will flow from gas to source in the reverse process and the process will be irreversible.

Example : As a matter of fact, reversible process is an ideal conception. The practical realisation is possible only when the process is very-very slow.

Joule Thomson effect is irreversible process. A fall of temperature occurs whether a gas crosses the porous plug in one direction or in the reverse direction. Similarly, electric resistance is irreversible, heat is produced always whatever be the direction of current flow.

(i) **Isothermal Expansion of a Gas** : Consider a gas enclosed in a non-conducting cylinder with a movable piston. Let the piston be weightless and frictionless. Suppose the cylinder is in thermal contact with a hot furnace at 100°C and the gas is in thermal equilibrium. When the load on the piston increases, then it moves down. Due to this, the piston works on the gas and the energy of gas increases and hence the temperature of the gas increases. If the process is very-slow, the amount of heat increased will be very small. Let the temperature of the gas increase by 0.01°C . Therefore the temperature of the gas becomes 100.01°C . In this position, the heat will flow from gas to the furnace due to temperature difference. On reversing the process, the piston moves slowly in backward direction. In this position, the work is done by the gas on the piston. To do this work the gas takes some energy from itself and hence its temperature falls. If the process is quite slow, then this fall in temperature will be infinitely small. Say the temperature of the gas becomes 99.99°C . In this position the heat will flow from furnace to the gas. Thus, if the process is quite slow, then the gas and furnace will always remain in equilibrium, and the heat ejected by the gas in direct process is the same as the heat absorbed by the gas during the reverse process. The condition described above can not be obtained in practice hence a very slow isothermal expansion is approximately reversible.

(ii) **Adiabatic Compression of a Gas** : If we take the cylinder which is perfectly non-conducting, *i.e.*, bottom is also non-conducting and the gas is compressed infinitesimally slowly, the compression is reversible. In practice, it is only approximately reversible.

(iii) **Transference of Heat from One Body to Another** : If heat flows from one body (hot) to another body (cold) then the process will be irreversible, because heat can not be transferred back from the cold body to the hot body.

(iv) **Production of Heat by Friction** : When a body moves on a surface then a part of its energy is spent to overcome the effect of friction between itself and surface. The energy spent is dissipated as heat. If the body is allowed to move on the surface in reverse direction its energy is again spent as before and can not be recovered. Hence the process is irreversible.

(v) **Operation of an Engine on the Carnot's Cycle** : Since the Carnot's cycle is perfectly reversible therefore entropy remains constant and hence process is reversible.

(vi) **Joule-Thomson Effect** : When a gas passes from higher pressure to lower pressure then there is a fall in its temperature. This effect is known as Joule-Thomson effect. If the process is reversed then energy lost in direct process is not recovered but the gas will have to further spend its energy and will cool more. Thus the Joule-Thomson effect is an irreversible process.

(vii) **Joule Expansion of a Perfect Gas** : In this process, the volume of a perfect gas increases at constant temperature. To bring the gas in its initial position, external work has done, which converts into heat. To do this work the required heat is to be taken from the gas, which is impossible. Hence the process is irreversible.

(viii) **A Resistor Carrying Current and Kept at a Constant Temperature by a Stream of Running Water** : When current is passed in the resistor then heat is produced. This heat is not fully converted into electrical energy and so the process is irreversible.

• STUDENT ACTIVITY

3. Distinguish between reversible and irreversible processes.

4. To which category (reversible or irreversible) the following processes belong and why ?

- (i) Adiabatic compression of a gas.
- (ii) Production of heat of friction.

• 3.5. HEAT ENGINE

Heat engine is a device which is used to convert heat continuously into work. It consists of three essential parts :

- (i) Hot body or source for the supply of heat at high temperature.
- (ii) Cold body or sink, for the rejection of heat at lower temperature.
- (iii) The working substance which can absorb heat from the source.

The working substance takes heat from the source, converts a part of it into work and rest is given to sink. This process is known as 'cycle' because the working substance returns to its original state.

Efficiency : Consider Q_1 is the amount of heat absorbed by the working substance, a part of it is used in doing work W and rest of it, Q_2 is given to sink. The efficiency of engine is defined as "the ratio of the work to the heat Q_1 ". It is denoted by η . Thus

$$\eta = \frac{W}{Q_1}$$

The heat given to sink is

$$Q_2 = Q_1 - W$$

$$W = Q_1 - Q_2$$

Therefore,

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\boxed{\eta = 1 - \frac{Q_2}{Q_1}}$$

This is the required expression for the efficiency of the heat engine. From this expression it is clear that the efficiency of heat engine will be 100%, if $Q_2 = 0$, i.e., heat given to sink must be zero, which is not possible in practice. Thus, the engine can not convert all the heat into work without any sink.

Indicator Diagram : The graphical representation of any physical process on the pressure-volume diagram is known as indicator diagram. It is used in the study of engine and to calculate the amount of work obtained from it.

Consider one gram mole of a gas enclosed in a cylinder with a frictionless piston. Let A be the area of cross-section of the piston. Now the gas is allowed to expand through an elementary distance dx at a pressure P , then the amount of work done is

$$dW = \text{force exerted on the piston} \times \text{displacement}$$

$$dW = P \times A \times dx$$

$$dW = PdV$$

$$[\because Adx = dV]$$

The work done for an expansion from an initial state $[P_1, V_1]$ to the final state $[P_2, V_2]$ is

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

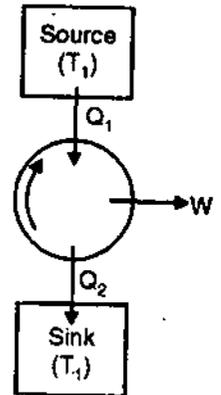


Fig. 2

In the fig. (3), *A* and *B* are the initial and final states, respectively. The intermediate changes are represented by the line *AB*.

Consider a point *M*, at which the pressure of the gas is *p*. Let the volume increase by infinitely small amount *dV* to the point *N*. In this position, the small work done is *PdV* shown by the strip *MNSR*. The total work done when the gas expands from initial state to final state is

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

From above we conclude that the area bounded on the indicator diagram gives the amount of work done. This result is used in the performance of a heat engine.

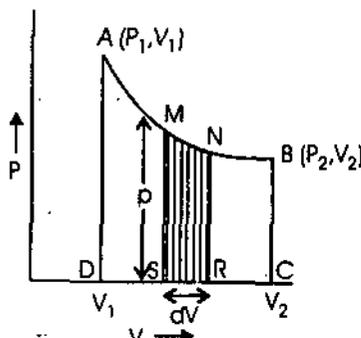


Fig. 3

• 3.6. CARNOT'S HEAT ENGINE (Reversible heat engine)

Heat engine is a device which is used to convert heat into work continuously. Carnot, on the basis of theoretical investigations, developed a plan of an ideal engine, which should be free from all types of imperfection of an actual engine and hence its efficiency should be 100%. This can never be achieved in practice. But the importance of this is that with the help of this the efficiency of other engines can be compared.

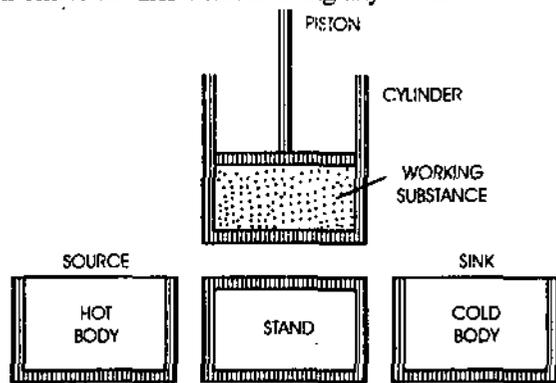
This engine consists of the following four parts as shown in fig. (4).

(i) The working substance is contained in a cylinder with perfectly non-conducting walls and provided with a non-conducting frictionless piston, the bottom of the cylinder being perfectly conducting.

(ii) A hot body of infinitely large heat capacity at a constant temperature T_1 . It is called 'source'.

(iii) A cold body of infinitely large heat capacity at a constant temperature T_2 . It is called 'sink'.

(iv) A perfectly heat-insulating stand. The cylinder may be placed on any of the three bodies and can be moved from one to another without doing any work.



The working substance is imagined to go through a cycle of four processes, known as the "Carnot's cycle."

Carnot's Cycle : The cycle of operations is shown in the indicator diagram. Let *A* be the initial state of the working substance, which is shown in fig. 5.

Process I : Let at point *A*, the working substance be in its initial state, at which the pressure and volume are P_1 and V_1 , respectively. Now the cylinder is placed on the source. Due to this, the piston moves slowly in the upward direction such that the gas expands. In the isothermal expansion, the temperature of the gas falls but due to the contact with source, a certain amount of heat Q_1 is taken from the source to maintain the temperature at T_1 °K. The final state (P_2, V_2) of the gas is shown by a point *B* in the fig. 4. In this position, the amount of work done by the gas is

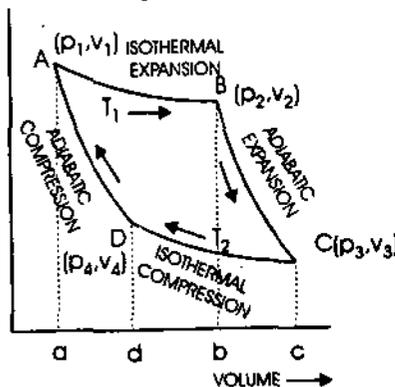


Fig. 5

$$\begin{aligned}
 Q_1 = W_1 &= \int_{V_1}^{V_2} P dV = RT_1 \int_{V_1}^{V_2} \frac{dV}{V} = RT_1 [\log_e V]_{V_1}^{V_2} \\
 &= RT_1 \log_e \frac{V_2}{V_1} = \text{area } ABba \quad \dots(1)
 \end{aligned}$$

Process II : Now the cylinder is removed from the source and placed on the stand. In this position, the piston moves further adiabatically until the temperature of the gas becomes equal to the temperature of the sink, *i.e.*, T_2 . This is shown by the curve BC , in this process the pressure and volume become P_2 and V_2 , respectively. The work done W_2 is

$$W_2 = \int_{V_1}^{V_2} P dV = \frac{R(T_1 - T_2)}{\gamma - 1} = \text{area } BCab \quad \dots(2)$$

Process III : Now the cylinder is removed from the stand and placed on the sink. In this position, the piston moves in the downward direction, the gas is compressed to a point D , where the pressure and volume become P_4 , V_4 . In this process the workdone is

$$Q_2 = W_3 = - \int_{V_3}^{V_4} P dV = RT_2 \log \frac{V_3}{V_4} = \text{area } DCcd \quad \dots(3)$$

Process IV : Finally, the cylinder is placed on the stand again and the piston is further lowered such that the gas undergoes a slow adiabatic compression. The heat generated in this process will increase the temperature of the gas. When the pressure and volume correspond with the point A , then the compression is stopped. The temperature of the gas will be T_1 .

The work done W_4 on the gas is

$$W_4 = - \int_{V_4}^{V_1} P dV = \frac{R(T_1 - T_2)}{\gamma - 1} = \text{area } ADda \quad \dots(4)$$

The net workdone is $= W_1 - W_3$

Quantity of heat absorbed by the gas

$$= Q_1 - Q_2 = W_1 - W_3$$

Therefore, the efficiency of the cycle is

$$\begin{aligned}
 \eta &= \frac{\text{heat converted into work}}{\text{heat drawn from the source}} \\
 &= \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \quad \dots(5)
 \end{aligned}$$

$$\begin{aligned}
 \therefore \frac{Q_2}{Q_1} &= \frac{W_3}{W_1} = \frac{RT_2 \log \frac{V_3}{V_4}}{RT_1 \log \frac{V_2}{V_1}} \\
 &= \frac{T_2 \log \frac{V_3}{V_4}}{T_1 \log \frac{V_2}{V_1}} \quad \dots(6)
 \end{aligned}$$

For adiabatic process, we have

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

$$\text{or} \quad \frac{T_1}{T_2} = \left(\frac{V_3}{V_2} \right)^{\gamma-1} \quad \dots(7)$$

and

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

$$\frac{T_1}{T_2} = \left(\frac{V_4}{V_1} \right)^{\gamma-1} \quad \dots(8)$$

From equations (7) and (8), we get

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4} \quad \dots(9)$$

So by equation (6), we get

$$\frac{Q_2}{Q_1} = \frac{T_2 \log \frac{V_2}{V_1}}{T_1 \log \frac{V_2}{V_1}} \quad \text{[from (9)]}$$

$$= \frac{T_2}{T_1} \quad \dots(10)$$

From equations (5) and (10), we get

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

This is the required expression for the efficiency of heat engine working between temperature T_1 and T_2 .

From the above expression, it is clear that **the Carnot's reversible engine is independent of the working substance and depends only on the absolute temperatures of the sink and the source.**

The Carnot's engine cannot be realised in practice due to the following two reasons :

(i) It makes full use of the available temperature difference, *i.e.*, heat is absorbed at a constant temperature as well as rejected at a constant temperature. In actual engine, the temperature of the hot body falls as it gives heat and that of cold body rises as it receives the heat.

(ii) It is perfectly reversible in its action. If the cycle is reversed the working substance will take an amount Q_2 of heat from the sink and gives out an amount Q_1 to the source. The engine thus acts as a refrigerator.

• 3.7. CARNOT IDEAL REFRIGERATOR

Refrigerator is a device which is used to transfer heat from cold body to hotter body with the help of external agency or it is a heat engine running into backward direction.

Carnot's cycle is perfectly reversible. It can work as both the heat engine and the refrigerator. When it works as a heat engine, it takes heat Q_1 from the source at a higher temperature T_1 a part of it is converted in work W and rest heat Q_2 is given to the body at a lower temperature T_2 . But when it works as a refrigerator, the working substance takes heat Q_2 from the cold body (T_2), an external work is done on it, and rejects larger amount of heat Q_1 to the hotter body at temperature T_1 . It continues to transfer heat from a cold body to hot body and hence cold body is cooled more.

Let us consider that Q_2 is the heat taken from the cold body at temperature T_2 , W is the net work done on it and Q_1 is the heat given to hotter body at temperature T_1 , then

$$\begin{aligned} Q_1 &= Q_2 + W \\ W &= Q_1 - Q_2 \\ W &= Q_2 \left(\frac{Q_1}{Q_2} - 1 \right) \end{aligned}$$

We know that,

$$\begin{aligned} \frac{Q_1}{Q_2} &= \frac{T_1}{T_2} \\ \therefore W &= Q_2 \left(\frac{T_1}{T_2} - 1 \right) \\ W &= Q_2 \left(\frac{T_1 - T_2}{T_2} \right) \end{aligned}$$

This is the required work done which is used to run the refrigerator.

(b) **Coefficient of Performance** : It is defined as "the ratio of the heat taken from the cold body to the work needed to run the refrigerator." That is,

$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

or

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

Efficiency of Carnot engine is given by

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

and coefficient of performance is given by

$$K = \frac{T_2}{T_1 - T_2}$$

or

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

or

$$\eta = \frac{1}{K + 1}$$

This is the required relation between efficiency and coefficient of performance.

• 3.8. CARNOT'S THEOREM

According to this theorem.

(i) No engine can be more efficient than a reversible engine working between the same temperatures, and

(ii) All reversible engines working between the same temperatures, are equally efficient whatever be the working substance.

Let us consider I and R as two irreversible and reversible engines, respectively. These two engines are so adjusted that they perform equal amount of work. Let the reversible engine R take heat Q_1 from the source, a part of it is converted into work W and rest $Q_1 - W$ is given to sink. So its efficiency will be $\frac{W}{Q_1}$. Similarly, let the irreversible engine I take Q_1' heat from the source, the same amount of work W is obtained and rest $(Q_1' - W)$ is given to sink. So its efficiency will be $\frac{W}{Q_1'}$.

If the irreversible engine I is more efficient than the reversible engine R , then

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

or

$$Q_1 > Q_1'$$

or

$$(Q_1 - Q_1') > 0$$

which is a positive quantity.

Now the two engines are coupled together in such a way that I drives R in the backward direction. In this position R acts as a refrigerator and takes $(Q_1 - W)$ heat from the sink, the work W is done on it and rejects Q_1 heat to the source. Since all the work needed to run the refrigerator R is supplied by the irreversible engine I , so the two engines constitute a self acting machine. The quantity of heat taken from the sink is

$$\begin{aligned} &= (Q_1 - W) - (Q_1' - W) \\ &= Q_1 - Q_1' \end{aligned}$$

which is a positive quantity. This is also the net amount of heat rejected to the source. Therefore, the effect of this coupled device is to transfer a quantity $(Q_1 - Q_1')$ from the sink to the source without any external source. This is the violation of the second law of thermodynamics. Hence our original assumption that irreversible engine is more efficient than a reversible engine is wrong.

Now we have to prove the second part. For this, consider reversible engines I and R are working between the source and sink. Let I be driving R backward. In this position I can not be more efficient than R . If R is driving I backward, then R cannot be more efficient than I . Hence we can say that the two engines are equally efficient. Thus the efficiency of a reversible engine depends only upon the temperature of source and sink and is independent of the working substance.

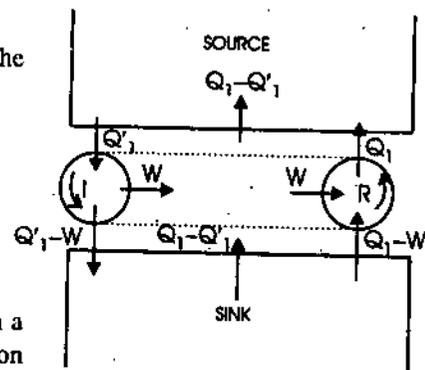


Fig. 6

• 3.9. ABSOLUTE SCALE OF TEMPERATURE

The scale of an ordinary thermometer depends upon the physical property (like thermal expansion, electric resistance and thermo e.m.f. etc.) of the substance used in thermometer. Since there is no physical property which varies continuously with temperature, these scales are arbitrary.

"A temperature scale which is independent of the properties of any particular substance is known as absolute scale of temperature."

According to Carnot's theorem, the efficiency of a reversible engine is independent of the working substance and depends only on the two temperatures between which it is working. Using this hint, Lord Kelvin defined a temperature scale which does not depend upon the properties of any particular substance. This is the "Kelvin's absolute thermodynamic scale of temperature."

Let the temperatures of source and sink measured by any scale are T_1 and T_2 respectively. Let the reversible engine takes heat Q_1 from the source giving out heat Q_2 to sink. The efficiency of this engine is

$$\eta = 1 - \frac{Q_2}{Q_1} = f(T_1, T_2)$$

where f is an unknown function.

These temperatures (T_1 and T_2) are measured on an arbitrary scale.

From above it is clear that $\frac{Q_2}{Q_1}$ or $\frac{Q_1}{Q_2}$ must be a function of T_1 and T_2 .

$$\text{Thus, } \frac{Q_1}{Q_2} = f'(T_1, T_2) \quad \dots(1)$$

where f' is some other unknown function $f'(T_1, T_2)$. Depending upon the temperatures of source and sink only is naturally a universal function for all reversible engines working between the same two temperatures.

Consider another Carnot's cycle which absorbs Q_2 heat from the source at T_2 and rejects Q_3 heat at lower temperature T_3 to the sink. Then

$$\frac{Q_2}{Q_3} = f'(T_2, T_3) \quad \dots(2)$$

Now let us consider a third engine by coupling the first two engines, *i.e.*, heat rejected by the first engine, Q_2 is absorbed by the second engine. Thus the existence of Q_2 disappears when we consider this third engine. Thus the substance absorbs Q_1 heat from source at temperature T_1 and rejects Q_3 heat to the sink at temperature T_3 . Then we can write

$$\frac{Q_1}{Q_3} = f'(T_1, T_3) \quad \dots(3)$$

Multiplying (1) and (2)

$$\frac{Q_1}{Q_2} \times \frac{Q_2}{Q_3} = \frac{Q_1}{Q_3} = f'(T_1, T_2) \times f'(T_2, T_3)$$

$$f'(T_1, T_3) = f'(T_1, T_2) \times f'(T_2, T_3)$$

$$\text{or } f'(T_1, T_2) = \frac{f'(T_1, T_3)}{f'(T_2, T_3)} \quad \dots(4)$$

Since T_3 is not appearing in left hand side therefore in right hand side T_3 should be cancelled in numerator and denominator. This is possible only when the function f' change to ϕ . Thus, the equation (4) becomes

$$f'(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)} \quad \dots(5)$$

From equations (1) and (5),

$$\frac{Q_1}{Q_2} = \frac{\phi(T_1)}{\phi(T_2)} \quad \dots(6)$$

Since $Q_1 > Q_2$, function $\phi(T_1) > \phi(T_2)$. Thus $\phi(T)$ is a lower function of T . For example, $\phi(T)$ may be some multiple of T . Thus $\phi(T)$ may be taken to represent a temperature τ on a new scale and we have

$$\frac{Q_1}{Q_2} = \frac{\tau_1}{\tau_2} \quad \dots(7)$$

The right hand side of this equation is defined as the ratio of the two thermodynamic temperatures or Kelvin temperatures. The thermodynamic scale is therefore, defined as :

“The ratio of two temperatures on the thermodynamic scale is same as the ratio of the heat absorbed and rejected by a Carnot’s engine operating between reservoirs at these temperatures

$$\frac{\tau_1 - \tau_2}{\tau_2} = \frac{Q_1 - Q_2}{Q_2} = \frac{W}{Q}$$

Thus the difference of two temperatures may be measured in terms of work obtained from a reversible engine working between these two temperatures. This new scale is therefore also known as the work scale of temperature.

Zero of the Absolute Scale (Absolute Zero) : The efficiency of reversible engine on the thermodynamic scale is given by

$$\eta = 1 - \frac{\tau_2}{\tau_1}$$

If we consider an engine working between steam point (τ_1) and absolute zero ($\tau_2 = 0$)

$$\eta = 1 - \frac{\tau_2}{T_1 \text{ (steam)}}$$

$$\eta = 1$$

i.e., the engine has efficiency equal to 1. Similarly if the engine is working between ice point and absolute zero, the efficiency will be

$$\eta' - 1 = \frac{\tau_2}{T_1 \text{ (ice)}} = 1$$

But $\eta = 1 - \frac{Q_2}{Q_1}$

$\therefore 1 = 1 - \frac{Q_2}{Q_1}$

or $Q_2 = 0$

This means that if the sink is at the temperature of zero degree absolute, no heat is rejected and whole of the energy is used in doing work. In this position, the efficiency will be 100%. Thus absolute zero is that temperature of the sink at which no heat is rejected to it.

But according to second law of thermodynamics, no engine can have cent per cent efficiency ($\eta = 100\%$). Thus the absolute zero temperature is not possible.

This is also known as **third law of thermodynamics**.

Comparison of Absolute Scale and Perfect (Ideal) Gas Scale :

We know that in Carnot’s engine with perfect gas as working substance

$$\eta = 1 - \frac{Q_2}{Q_1}$$

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

$\therefore 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

or $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$... (1)

These temperatures were supposed to be in perfect gas scale. In an absolute thermodynamic scale, we know

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \dots (2)$$

Here, the same Carnot’s engine is used in both cases to absorb the same heat Q_1 and rejects heat Q_2 .

Thus from eqns. (1) and (2),

$$\frac{T_2}{T_1} = \frac{\tau_2}{\tau_1} \dots (3)$$

Let the engine be working between steam and ice point then from equation (3),

$$\frac{T_s}{T_i} = \frac{\tau_s}{\tau_i}$$

or

$$\frac{T_s - T_i}{T_i} = \frac{\tau_s - \tau_i}{\tau_i} \quad \dots(4)$$

In both cases,

$$T_s - T_i = 100 - 0 = 100 \quad T_s = 100^\circ\text{C}$$

$$\tau_s - \tau_i = 100 - 0 = 100 \quad T_i = 0^\circ\text{C}$$

$$\frac{100}{T_i} = \frac{100}{\tau_i}$$

$$\boxed{T_i = \tau_i}$$

or

$$T_i + 100 = \tau_i + 100$$

$$\boxed{T_s = \tau_s}$$

i.e., the ice and steam points on the two scales are identical.

Now for a Carnot's engine working between the steam point and another general temperature

T ,

$$\frac{T_s}{T} = \frac{\tau_s}{\tau}$$

or

$$T = \tau$$

Thus, the thermodynamic temperature and perfect gas temperature are numerically equal to each other. Thus, the two scales are completely equivalent, *i.e.*, measurement of temperature on the two scales will give identical values.

• 3.10. ENTROPY

The concept of entropy was first given by Clausius. It is very important physical quantity like pressure, temperature, volume etc., which is used to study the behaviour of heat engines.

Let us consider a Carnot's cycle drawn at different temperatures T_1 , T_2 , T_3 etc. on the pressure volume diagram (fig. 7)

Let A and B be two adiabatic curves which cut the isotherms at a, and b, c and d, e and f. Consider a reversible cycle *abdc* working between the temperatures T_1 and T_2 . Let in this cycles the working substance takes Q_1 heat at temperature T_1 and rejects Q_2 heat at temperature T_2 .

We know
$$\eta = 1 - \frac{Q_2}{Q_1}$$

and

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

\therefore

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

or

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

or

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

Similarly, for cycle *cdfe*, working between temperatures T_2 and T_3 the working substance takes heat Q_2 at temperature T_2 and rejects heat Q_3 at temperature T_3 , then

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

Thus, we can write

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \dots \frac{Q}{T} = \text{constant.}$$

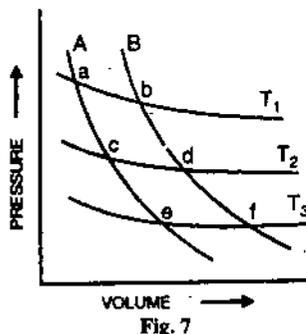


Fig. 7

From the above it is clear that quantity $\frac{Q}{T}$ remains constant. This quantity is known as 'entropy'

of the working substance. The quantity $\frac{Q}{T}$ is a definite thermal property of the working substance. Since there is no transference of heat during adiabatic path, so this quantity will be zero. In other words we can say that "the thermal property of the substance" which remains constant during an adiabatic change is termed as "entropy". We can not measure entropy absolutely, only change in the entropy of the substance can be measured.

Physical Significance : The entropy of a substance is real quantity and it is a definite function of the state of the body like pressure, temperature, volume or internal energy.

We have,

$$\text{Change in entropy} = \frac{\text{heat energy}}{\text{temperature}}$$

or change of entropy \times temperature = heat energy ... (1)

The gravitational potential energy is given by

$$\text{gravitational potential energy} \propto \text{mass} \times \text{height}$$

... (2)

From equations (1) and (2), it is clear that if the temperature is equivalent to height then entropy will be equivalent to mass or inertia. Hence entropy plays the same role in heat motion as mass plays in linear motion or moment of inertia plays in rotational motion.

Change of Entropy in a Reversible Process : Isentropic Process: Consider a Carnot reversible cycle ABCD as shown in the fig. 8. Let during the path AB the working substance takes heat at temperature T_1 so that its entropy increases by $\frac{Q_1}{T_1}$.

The paths BC and DA are adiabatic, so the change in entropy on these paths will be zero. During the path CD, the working substance gives heat Q_2 to the sink at temperature T_2 so that its entropy decreases by $\frac{Q_2}{T_2}$.

Thus net change of entropy during the complete cycle is

$$\Delta S = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$$

For reversible cycle, we have

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

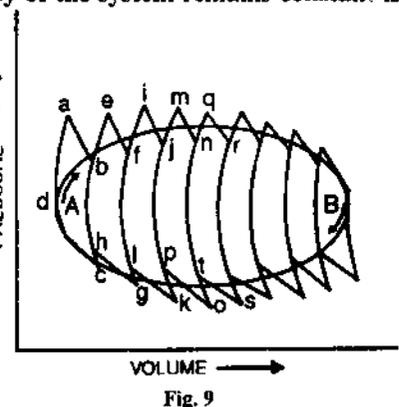
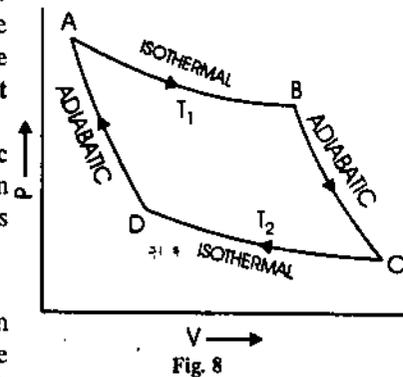
so

$$\Delta S = 0$$

Thus, the entropy of a system remains constant in reversible process. This is "Clausius theorem". Hence a reversible process in which the entropy of the system remains constant is known as "isentropic process."

Now we take a general case of any reversible cycle $A \rightarrow B \rightarrow A$ as shown in fig. 9. In fig. 9, a cycle is divided into many elementary Carnot cycles, *abcd*, *efgh*, *ijkl* etc. Let us imagine that the substance, instead of tracing the smooth curve $A \rightarrow B \rightarrow A$, traces successively the cycles *abcd*, *efgh*, *ijkl*, In this, the portions *bh*, *fl*, *jp*, *nt*, ... are traversed twice in reverse order and hence their effects are cancelled. The net effect of the entire process is due to the closed zig-zag path *abefi... ghcha*. Consider the heat taken by the substance to be positive while the heat Q_2 given up is negative, then we have

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



or
$$\Delta S = \frac{\delta Q_1}{T_1} + \frac{\delta Q_2}{T_2} = 0$$

or
$$\Delta S = \sum \frac{\delta Q}{T} = 0 \quad \dots(1)$$

Hence, the relation (1) is true for this zig-zag path.

In the case, when the adiabatics *ad, ec, ig, mk* etc. are quite close to each other then isothermals *ad, cd, ef, gh* etc., will be infinitely small. In this position, the path will coincide with the smooth curve *ABC*. Therefore for any reversible cycle we may write

$$\Delta S = \oint \frac{dQ}{T} = 0$$

Thus, the net change in the entropy for any reversible cycle is zero.

Change in Entropy in Irreversible Process : We know that the efficiency of a reversible engine is given by

$$\eta = 1 - \frac{Q_2}{Q_1}$$

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

and
$$1 - \frac{Q_2}{Q_1} < 1 - \frac{T_2}{T_1}$$

$$\therefore \frac{Q_2}{Q_1} > \frac{T_2}{T_1}$$

or
$$\frac{Q_2}{T_2} > \frac{Q_1}{T_1} \quad \dots(1)$$

Total increase in entropy

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

$$dS > 0 \quad \text{[From eqn. (1)]}$$

Thus, in an irreversible process, the entropy of whole system (System + Surroundings) always increases.

In general $dS_{(\text{universe})} \geq 0$

• 3.11. TEMPERATURE-ENTROPY (T-S) DIAGRAM

Carnot's cycle is formed by two reversible isothermal processes and two reversible adiabatic processes as shown in the fig. 10(a). When Carnot's cycle on P-V diagram, as shown in fig. 10(b) is plotted on T-S diagram then it assumes of rectangular shape.

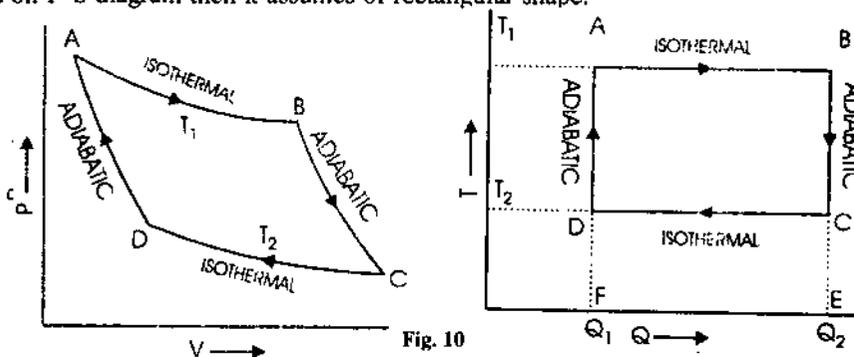


Fig. 10

On the path *AB*, the entropy of the working substance increases from S_1 to S_2 , while temperature remains constant. On the path *BC*, the entropy remains constant while the temperature falls from T_1 to T_2 . On *CD*, the entropy decreases from S_2 to S_1 at constant temperature T_2 .

Finally, on the path *DA* the temperature rises to T_1 at constant entropy S_1 . *T-S* diagram has various applications. For example, for engineers for the study of engines. **The area of the cycle on T-S diagram gives the available energy.**

(b) (i) Let the working substance takes heat Q_1 on path *AB* and rejects heat Q_2 on the path *CD*.

From
$$dQ = T dS$$

From the fig. 10 the heat extracted from source is

$$Q_1 = T_1 (S_2 - S_1)$$

$$Q_1 = AF \times AB \\ = \text{Area } ABEF$$

(ii) Heat given to sink is

$$Q_2 = T_2 (S_2 - S_1)$$

$$Q_2 = DF \times DC$$

$$Q_2 = \text{Area } DCEF$$

(iii) Heat converted into work is

$$W = Q_1 - Q_2$$

$$= \text{Area } ABEF - \text{Area } DCEF$$

$$= \text{Area } ABCD$$

• 3.12. PRINCIPLE OF INCREASE OF ENTROPY

In any thermodynamical process, there will be changes of entropy in the system as well as its surroundings. In this position the total change in the entropy of the system + surroundings is known as entropy change of the universe.

Principle of increase of entropy states, that **whenever any physical or chemical process occurs; then the entropy of the universe increases and for reversible process, the entropy remains constant.**

(i) **Entropy change of the universe due to reversible process:** Here we have to show that the entropy of the universe due to the reversible process is zero. For this consider the Carnot cycle. During isothermal expansion, the working substance takes heat Q_1 from the source at temperature T_1 . Due to this, the increase in entropy of the working substance is $\frac{Q_1}{T_1}$. Thus, the net change in entropy of the universe during a reversible isothermal process is zero. During adiabatic processes, the change in entropy will be zero.

For whole cycle, the loss of entropy of the source is $\frac{Q_1}{T_1}$ and gain in entropy of the sink is $\frac{Q_2}{T_2}$ so that the net increase in entropy is

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1} = 0 \quad \left[\because \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \right]$$

Thus, the entropy of the whole system remains constant.

(ii) **Entropy change of the universe due to irreversible process:** When the transference of heat takes place due to conduction, then this process is known as irreversible process. Let A and B be two bodies, A remains at higher temperature T_1 and B remains at lower temperature T_2 , i.e., $T_1 > T_2$. Let a quantity dQ be transferred from hot body A at temperature T_1 to cold body at temperature T_2 . In this position, the loss of entropy of A is $\frac{dQ}{T_1}$ and the gain in entropy of B is $\frac{dQ}{T_2}$.

Thus, the net change in entropy is

$$dS = \frac{dQ}{T_2} - \frac{dQ}{T_1}$$

or

$$dS > 0 \quad [\because T_1 > T_2]$$

From this, it is clear that **the entropy during irreversible process always increases.**

Principle of Degradation of Energy : According to this principle “**the available energy of the universe tends to zero.**” This principle also states that, whenever an irreversible process takes place, then a certain amount of energy of the universe is converted from a form in which it was available for work into a form in which it is unavailable for work.

For Carnot engine, the working substance takes heat Q_1 from hot body at temperature T_1 and rejects heat Q_2 to a cold body at temperature T_2 . The quantity $(Q_1 - Q_2)$ is converted into work and this quantity of heat is known as “available energy.” Thus, available energy is

$$Q_1 - Q_2 = Q_1 \left(1 - \frac{Q_2}{Q_1} \right) = Q_1 \left(1 - \frac{T_2}{T_1} \right) \quad \left[\because \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \right]$$

If the temperature of the cold body is T_0 then the available energy is

$$Q_1 \left(1 - \frac{T_0}{T_1} \right)$$

Let us consider the irreversible process in which body takes Q heat from a body at temperature T_1 and rejects to another body having temperature T_2 ($T_1 > T_2$) then available energy to start with

is $Q \left(1 - \frac{T_0}{T_1} \right)$ After the transfer it becomes $Q \left(1 - \frac{T_0}{T_2} \right)$

Thus, the loss of available energy is

$$\begin{aligned} &= Q \left(1 - \frac{T_0}{T_1} \right) - Q \left(1 - \frac{T_0}{T_2} \right) \\ &= Q \left(\frac{T_0}{T_2} - \frac{T_0}{T_1} \right) \\ &= T_0 \left(\frac{Q}{T_2} - \frac{Q}{T_1} \right) \\ &= T \cdot dS \end{aligned}$$

where $dS = \left(\frac{Q}{T_2} - \frac{Q}{T_1} \right)$ is the increase in entropy.

Since $T_1 > T_2$ therefore, the entropy is increasing while the available energy is decreasing. Since processes in nature are irreversible, the available energy of the universe is continually decreasing. This is known as the 'degradation of energy'. This principle of 'degradation' can now be stated as :

"Whenever an irreversible process takes place, certain amount of energy which could have been utilised for doing useful work changes to a form in which it becomes unavailable".

• 3.13. ENTROPY OF A PERFECT GAS

Consider 1 mole of a perfect gas at pressure P , temperature T and volume V . If dQ amount of heat is supplied to gas, then increase in energy is given by

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

or

$$S = \int \frac{dQ}{T}$$

From the first law of thermodynamics

$$dQ = dU + dW$$

∴

$$S = \int \frac{dU + dW}{T}$$

and

$$dU = mc \cdot dT$$

$$dU = 1 \cdot C_V dT \text{ and } dW = PdV = RT \cdot \frac{dV}{V}$$

Hence

$$S = \int \frac{C_V \cdot dT}{T} + R \int \frac{dV}{V} \quad \dots(1)$$

(i) If temperature and volume of the gas change from T_1, V_1 to T_2, V_2 then from equation (1) change in entropy of the gas is

$$dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

or

$$dS = C_V \log_e \left(\frac{T_2}{T_1} \right) + R \log_e \left(\frac{V_2}{V_1} \right)$$

$$dS = C_V \log_e \left(\frac{T_2}{T_1} \right) + (C_P - C_V) \log_e \left(\frac{V_2}{V_1} \right)$$

This is the change in entropy in terms of temperature, volume and specific heat.

(ii) To express the entropy in terms of temperature and pressure, eliminate V or dV from equation (1)

From $PV = RT$

$$PdV + VdP = R \cdot dT$$

$$dV = \frac{(RdT - VdP)}{P}$$

From (1)

$$S = \int C_V \frac{dT}{T} + \int \frac{P(RdT - VdP)}{PT}$$

$$= \int C_V \frac{dT}{T} + \int \frac{(RdT - VdP)}{T}$$

$$= \int C_V \frac{dT}{T} + \int R \left(\frac{PT}{T} - \frac{dP}{P} \right)$$

$$S = \int C_V \frac{dT}{T} + (C_P - C_V) \left(\frac{dT}{T} - \frac{dP}{P} \right)$$

$$= \int C_P \frac{dT}{T} - \int (C_P - C_V) \frac{dP}{P} \quad \dots(2)$$

If temperature and pressure of the gas changes from T_1, P_1 to T_2, P_2 then from equation (2) change in entropy of the gas is

$$S = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} (C_P - C_V) \frac{dP}{P}$$

$$S = C_P \log_e \frac{T_2}{T_1} - (C_P - C_V) \log_e \frac{P_2}{P_1}$$

This is the change in entropy in terms of temperature, volume and specific heat.

(iii) To express the entropy in terms of pressure and volume, we have to eliminate T from (1),

we have $T = \frac{PV}{R}$.

$$\therefore dT = \frac{PdV + VdP}{R}$$

$$\therefore S = \int C_V \frac{(PdV + VdP)}{RT} + \int \frac{PdV}{T}$$

$$= \int C_V \frac{(PdV + VdP)}{RT} + \int \frac{PdVR}{PV}$$

$$= \int C_V \left(\frac{dV}{V} + \frac{dP}{P} \right) + \int (C_P - C_V) \frac{dV}{V}$$

$$= \int C_V \frac{dP}{P} + \int C_P \frac{dV}{V} \quad \dots(3)$$

If pressure and volume of the gas change from P_1, V_1 to P_2, V_2 then from equation (3), change in entropy of the gas is

$$S = \int_{P_1}^{P_2} C_V \frac{dP}{P} + \int_{V_1}^{V_2} C_P \frac{dV}{V}$$

$$S = C_V \log_e \frac{P_2}{P_1} + C_P \log_e \frac{V_2}{V_1}$$

This is the change in entropy in terms of pressure, volume and specific heat.

• 3.14. ENTROPY OF A SYSTEM

Here, we have to determine the expression for the entropy when 1 gram of ice at temperature T_1 changes into steam at temperature T_2 . Let L_1 and L_2 be the latent heat of the ice and steam, respectively.

The change in entropy is given by

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

(i) When ice at temperature T_1 changes into water at temperature T_1 , then the change in entropy is

$$= \frac{L_1}{T_1}$$

(ii) When this water at temperature T_1 changes into water at temperature T_2 , then the change in entropy is

$$\begin{aligned} &= \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{1 \times C \times dT}{T} \\ &= C \log_e \frac{T_2}{T_1} \end{aligned}$$

where C is the specific heat of water.

(iii) When water at T_2 changes into vapour at T_2 , then the change in entropy will be

$$= \frac{L_2}{T_2}$$

Therefore the net change in entropy is

$$= \frac{L_1}{T_1} + C \log_e \frac{T_2}{T_1} + \frac{L_2}{T_2}$$

This is the required expression for the change in entropy of the system.

• 3.15. RELATION BETWEEN ENTROPY AND MAXIMUM PROBABILITY

Ans. We know that entropy is connected with probability. Let S be the entropy and W be the maximum probability of the system in a definite state, then we can write,

$$S = f(W) \quad \dots(1)$$

Consider two systems A and B of entropies S_1 and S_2 , respectively. The entropy of the combined system will be

$$S = S_1 + S_2 \quad \dots(2) \text{ [}\because \text{entropy is additive]}$$

The probability of the combined system which consists of two entirely independent systems is

$$W = w_1 w_2 \quad \dots(3)$$

where w_1 and w_2 are the probabilities of different systems.

Again

$$\text{and } \left. \begin{aligned} S_1 &= f(w_1) \\ S_2 &= f(w_2) \end{aligned} \right\} \quad \dots(4)$$

Putting equations (1), (3) and (4) in equation (2) we get

$$f(w_1 w_2) = f(w_1) + f(w_2) \quad \dots(5)$$

Differentiating equation (5) with respect to w_1 , keeping w_2 constant we get

$$w_2 f'(w_1 w_2) = f'(w_1) \quad \dots(6)$$

Also differentiating with respect to w_2 , keeping w_1 constant, we get

$$w_1 f'(w_1 w_2) = f'(w_2) \quad \dots(7)$$

From equations (6) and (7), we get

$$\frac{w_2}{w_1} = \frac{f'(w_1)}{f'(w_2)}$$

$$\text{or } w_1 f'(w_1) = w_2 f'(w_2) = k \quad \dots(8)$$

where k is a constant.

From equation (8), we get

$$f'(w_1) = \frac{k}{w_1}$$

$$f'(w_2) = \frac{k}{w_2}$$

On integrating these expressions, we get

$$\int f'(w_1) dw_1 = \int \frac{k}{w_1} dw_1 + C$$

$$\text{and } \int f'(w_2) dw_2 = \int \frac{k}{w_2} dw_2 + C$$

$$\text{or} \quad f(w_1) = k \log w_1 + C$$

$$\text{and} \quad f(w_2) = k \log w_2 + C$$

In general we can write,

$$f(w) = k \log W + C$$

$$\text{or} \quad S = k \log W + C \quad \dots(9)$$

Where C is a constant of integration. In case of perfect order $W = 1$ and $S = 0$, so that $C = 0$. Therefore equation (9) gives

$$S = k \log W$$

This is the desired relation between entropy and maximum probability.

• SUMMARY

- Physical quantity which gives the direction of the flow of heat is known as temperature.
- The cyclic integral of heat is equal to the cyclic integral of work during cyclic process for closed system.
- The graphical representation of any physical process on the pressure-volume diagram is known as indicator diagram.
- Carnot's reversible engine is independent of the working substance and depends only on the absolute temperature of the sink and the source.
- The entropy of a system remains constant in reversible process, this is called "Clausius theorem".
- $S = k \log W + C$, where S be the entropy and W be the max. probability and C is a constant of integration.

• TEST YOURSELF

1. State and explain the zeroth law of thermodynamics and relate this law with the concept of temperature.
2. What do you understand by a heat engine and its efficiency? What is an indicator diagram?
3. Describe the working of the Carnot's reversible heat engine and find an expression for its efficiency.
4. State and prove Carnot's theorem.
5. What is an absolute scale of temperature? Show that this scale agrees with the ideal gas scale.
6. Calculate the efficiency of Carnot's engine operating between 125°C and 15°C .
Ans. 27.6%.
7. A Carnot's engine has an efficiency of 50% when the sink temperature is 17°C . What must be the change in its source temperature for making efficiency 60%?
Ans. 145°C .
8. What do you understand by the term entropy? Calculate the change in entropy in reversible and irreversible processes.
9. Show that the entropy of the universe tends to the maximum.
10. Derive an expression for the entropy of a perfect gas in terms of its pressure, volume and specific heat.
11. During an isothermal process, the quantity remains constant :
(a) temperature (b) pressure (c) volume (d) all of these
12. During an adiabatic process, the quantity remains constant :
(a) Temperature (b) Volume (c) Internal energy (d) None of the above
13. For the adiabatic process of an ideal gas, the relation between pressure and volume is given by :
(a) $pV = \text{constant}$ (b) $p^\gamma V = \text{constant}$
(c) $pV^\gamma = \text{constant}$ (d) none of the above
14. In free expansion :
(a) no heat enters or leave the system
(b) no work is done by or on the system
(c) both of (a) and (b)
(d) none of the above
15. The efficiency of a Carnot's engine is given by :
(a) $\frac{\text{Output}}{\text{input}}$ (b) $1 - \frac{Q_2}{Q_1}$ (c) $1 - \frac{T_2}{T_1}$ (d) All of these

16. For a Carnot's engine :
(a) $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ (b) $\frac{Q_1}{Q_2} = \frac{T_2}{T_1}$ (c) both of (a) and (b) (d) none of these
17. The change in entropy of a system is defined by :
(a) Q/T (b) p/V (c) VT (d) none of these

ANSWERS

11. (a) 12. (d) 13. (c) 14. (c) 15. (d) 16. (a) 17. (a)



MAXWELL'S RELATIONS

STRUCTURE

- Perfect Differentials
- Maxwell's Thermodynamic Relations
- Applications of Maxwell's Relations
- Joule-Thomson Effect
 - Student Activity
- Thermodynamic Functions
- Enthalpy
- Isenthalpic Curve
 - Student Activity
- Clausius-Clapeyron Equation (First Latent Heat Equation)
- Clausius' Latent Heat Equation (Second Latent Heat Equation)
 - Summary
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- The Clausius-Clapeyron latent heat equation : $\frac{\delta P}{\delta T} = \frac{L}{T(V_2 - V_1)}$
- Expression of $\frac{E_s}{E_T} = \frac{C_p}{C_v}$
- The relation of $C_p - C_v = R \left(1 + \frac{2a}{RTV} \right)$
- The relation of $TdS = C_p dT - T \left(\frac{\delta V}{\delta T} \right)_P \cdot dP$.
- Internal energy or Intrinsic energy (U).
- Helmholtz Function.
- Explanation of negative specific heat of saturated water vapour at 100°C.

4.1. PERFECT DIFFERENTIALS

Let Z is a function of two independent variables x and y , i.e., $Z = f(x, y)$. Let these variables be along two axes perpendicular to each other. Any point on the diagram will be defined by the value of variables x and y . At point A , the quantity Z has a definite value. This shows that when x and y are specified, then the function Z is completely determined and the differential dZ is known as perfect differential. In this position, when we go from the point A to C by any path, then the value of Z changes by the same amount whatever path is chosen. If Z undergoes a cyclic change, then line integral or cycle integral $\oint dZ$ will be zero.

Now we have to determine the mathematical condition that must be satisfied for dz to be a perfect differential. Let the variables x and y change by infinitesimal amounts dx and dy , respectively. In the fig. 2, the rectangle $PQRS$ shows the change. Let the coordinates of P are (x, y) and the sides PS and PQ be dx and dy respectively. The coordinates of other points of rectangle are shown in figure.

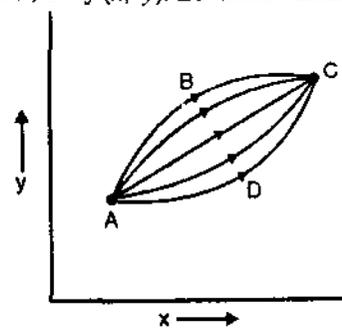


Fig. 1

To go from P to R , consider the path PQR . If the value of quantity at P is Z , then its value at Q is

$$\left(Z + \frac{\delta Z}{\delta y} dy \right)$$

The value of Z at R is

$$\left(Z + \frac{\delta Z}{\delta y} dy \right) + \frac{\delta}{\delta x} \left(Z + \frac{\delta Z}{\delta y} dy \right) dx \quad \dots(1)$$

For path PSR , the value of Z at S is

$$\left(Z + \frac{\delta Z}{\delta x} dx \right)$$

The value of Z at R is

$$\left(Z + \frac{\delta Z}{\delta x} dx \right) + \frac{\delta}{\delta y} \left(Z + \frac{\delta Z}{\delta x} dx \right) dy \quad \dots(2)$$

If dZ is perfect differential, then its value at R must be the same, whatever be the path i.e.,

$$\left(Z + \frac{\delta Z}{\delta y} dy \right) + \frac{\delta}{\delta x} \left(Z + \frac{\delta Z}{\delta y} dy \right) dx = \left(Z + \frac{\delta Z}{\delta x} dx \right) + \frac{\delta}{\delta y} \left(Z + \frac{\delta Z}{\delta x} dx \right) dy$$

$$\therefore Z + \frac{\delta Z}{\delta y} dy + \frac{\delta Z}{\delta x} dx + \frac{\delta^2 Z}{\delta x \delta y} dy dx = Z + \frac{\delta Z}{\delta x} dx + \frac{\delta Z}{\delta y} dy + \frac{\delta^2 Z}{\delta y \delta x} dx dy$$

$$\therefore \frac{\delta^2 Z}{\delta x \delta y} = \frac{\delta^2 Z}{\delta y \delta x}$$

Thus, dZ is a perfect differential.

If dZ is a perfect differential of a function (x, y) , then it may be written as

$$dZ = \left(\frac{\delta Z}{\delta x} \right)_y dx + \left(\frac{\delta Z}{\delta y} \right)_x dy.$$

Example : The thermodynamical state of a system can be described in terms of variables P , V , T and S . These variables change when the system goes from one state to another state. The differentials dP , dV , dT and dS are all perfect differentials.

(i) **Temperature :** From perfect gas equation

$$PV = RT$$

or

$$T = \frac{PV}{R} \quad \dots(3)$$

Differentiating with respect to V , taking P as constant $\frac{\delta T}{\delta V} = \frac{P}{R}$

Now differentiating with respect to P taking V as constant, we get

$$\frac{\delta}{\delta P} \left(\frac{\delta T}{\delta V} \right) = \frac{1}{R} \quad \dots(4)$$

Again from eqn. (3),

$$\frac{\delta T}{\delta P} = \frac{V}{R}$$

or

$$\frac{\delta}{\delta V} \left(\frac{\delta T}{\delta P} \right) = \frac{1}{R} \quad \dots(5)$$

From equations (4) and (5), we get

$$\frac{\delta}{\delta P} \left(\frac{\delta T}{\delta V} \right) = \frac{\delta}{\delta V} \left(\frac{\delta T}{\delta P} \right)$$

Hence dT is a perfect differential.

(ii) **Entropy :** From second law of thermodynamics, we have

$$dQ = TdS$$

The entropy S is property of the substance determined by the coordinates which define the particular state. In any reversible cycle, $\oint dS$ is zero, i.e., dS is a perfect differential.

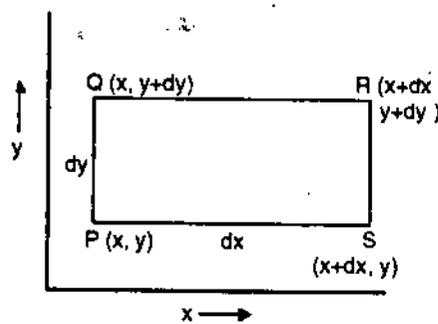


Fig. 2

4.2. MAXWELL'S THERMODYNAMIC RELATIONS

Maxwell's thermodynamic relations can be obtained by using the first and second laws of thermodynamics.

If a substance, for example, one gram molecule of a gas in container, absorbs heat dQ at constant pressure, a part of this heat is used in increasing the internal energy of the substance (dU) and rest is used in doing the work against external pressure P , then from first law of thermodynamics, we have

$$dQ = dU + PdV$$

or

$$dU = dQ - PdV \quad \dots(1)$$

According to the second law, if the substance absorbs a very small amount of heat dQ at temperature T , then the change in entropy dS is given by

$$dQ = TdS \quad \dots(2)$$

From equations (1) and (2), we get

$$dU = TdS - PdV \quad \dots(3)$$

Let U , S and V be the functions of two independent variables x and y i.e.,

$$U = U(x, y)$$

$$S = S(x, y)$$

and

$$V = V(x, y)$$

Since dU , dS and dV are perfect differentials, hence

$$dU = \left(\frac{\delta U}{\delta x}\right)_y dx + \left(\frac{\delta U}{\delta y}\right)_x dy$$

$$dS = \left(\frac{\delta S}{\delta x}\right)_y dx + \left(\frac{\delta S}{\delta y}\right)_x dy$$

and

$$dV = \left(\frac{\delta V}{\delta x}\right)_y dx + \left(\frac{\delta V}{\delta y}\right)_x dy$$

Putting these values in equation (3), we get

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

Equating the coefficient of dx and dy on both sides, we get

$$\left(\frac{\delta U}{\delta x}\right)_y = T \left(\frac{\delta S}{\delta x}\right)_y - P \left(\frac{\delta V}{\delta x}\right)_y \quad \dots(4)$$

and

$$\left(\frac{\delta U}{\delta y}\right)_x = T \left(\frac{\delta S}{\delta y}\right)_x - P \left(\frac{\delta V}{\delta y}\right)_x \quad \dots(5)$$

Since dU is a perfect differential, so

$$\frac{\delta}{\delta y} \left(\frac{\delta U}{\delta x}\right)_y = \frac{\delta}{\delta x} \left(\frac{\delta U}{\delta y}\right)_x$$

i.e.,

$$\frac{\delta}{\delta y} \left[T \left(\frac{\delta S}{\delta x}\right)_y - P \left(\frac{\delta V}{\delta x}\right)_y \right] = \frac{\delta}{\delta x} \left[T \left(\frac{\delta S}{\delta y}\right)_x - P \left(\frac{\delta V}{\delta y}\right)_x \right]$$

\therefore

$$\begin{aligned} \left(\frac{\delta T}{\delta y}\right)_x \left(\frac{\delta S}{\delta x}\right)_y + T \left(\frac{\delta^2 S}{\delta y \delta x}\right) - \left(\frac{\delta P}{\delta y}\right)_x \left(\frac{\delta V}{\delta x}\right)_y - P \left(\frac{\delta^2 V}{\delta y \delta x}\right) \\ = \left(\frac{\delta T}{\delta x}\right)_y \left(\frac{\delta S}{\delta y}\right)_x + T \left(\frac{\delta^2 S}{\delta x \delta y}\right) - \left(\frac{\delta P}{\delta x}\right)_y \left(\frac{\delta V}{\delta y}\right)_x - P \left(\frac{\delta^2 V}{\delta x \delta y}\right) \quad \dots(6) \end{aligned}$$

But

$$\left(\frac{\delta^2 S}{\delta y \delta x}\right) = \left(\frac{\delta^2 S}{\delta x \delta y}\right)$$

and

$$\left(\frac{\delta^2 V}{\delta y \delta x}\right) = \left(\frac{\delta^2 V}{\delta x \delta y}\right)$$

\therefore

$$\left(\frac{\delta T}{\delta y}\right)_x \left(\frac{\delta S}{\delta x}\right)_y - \left(\frac{\delta P}{\delta y}\right)_x \left(\frac{\delta V}{\delta x}\right)_y = \left(\frac{\delta T}{\delta x}\right)_y \left(\frac{\delta S}{\delta y}\right)_x - \left(\frac{\delta P}{\delta x}\right)_y \left(\frac{\delta V}{\delta y}\right)_x \quad \dots(7)$$

This is the general expression for Maxwell's thermodynamic relations. Now the following cases may arise.

(i) When, $x = T$ and $y = V$

$$\left(\frac{\delta T}{\delta x}\right) = 1 \quad \left(\frac{\delta V}{\delta y}\right) = 1$$

$$\left(\frac{\delta T}{\delta y}\right) = 0 \quad \left(\frac{\delta V}{\delta x}\right) = 0$$

Putting these values in equation (7), we get

$$0 = \left(\frac{\delta S}{\delta V}\right)_T - \left(\frac{\delta P}{\delta T}\right)_V$$

or

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V \quad \dots(8)$$

(2) When, $x = T$ and $y = P$, then

$$\left(\frac{\delta T}{\delta x}\right) = 1, \quad \left(\frac{\delta P}{\delta y}\right) = 1$$

$$\left(\frac{\delta T}{\delta y}\right) = 0, \quad \left(\frac{\delta P}{\delta x}\right) = 0$$

Putting these values in equation (7), we get

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P \quad \dots(9)$$

(3) When, $x = S$ and $y = V$, then

$$\left(\frac{\delta S}{\delta x}\right) = 1, \quad \left(\frac{\delta V}{\delta y}\right) = 1$$

$$\left(\frac{\delta S}{\delta y}\right) = 0, \quad \left(\frac{\delta V}{\delta x}\right) = 0$$

so, by equation (7), we get

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V \quad \dots(10)$$

(4) When, $x = S$ and $y = P$, then

$$\left(\frac{\delta S}{\delta x}\right) = 1, \quad \left(\frac{\delta P}{\delta y}\right) = 1$$

$$\left(\frac{\delta S}{\delta y}\right) = 0, \quad \left(\frac{\delta P}{\delta x}\right) = 0$$

So, by equation (7), we get

$$\left(\frac{\delta T}{\delta V}\right)_S = \left(\frac{\delta V}{\delta S}\right)_V \quad \dots(11)$$

Equations (8), (9), (10) and (11) are known as Maxwell's four thermodynamic relations.

• 4.3. APPLICATIONS OF MAXWELL'S RELATIONS

(i) Prove the thermodynamic relation

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

and hence prove the Clausius Clapeyron equation

$$\frac{\delta P}{\delta T} = \frac{L}{T(V_2 - V_1)}$$

Proof : $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$ is the Maxwell's first relation. This has proved in previous question.

We know that

$$\delta Q = T\delta S$$

$$\delta S = \frac{\delta Q}{T}$$

or

Put in above relation, we get

$$\left(\frac{\delta Q}{\delta V}\right)_T = T \left(\frac{\delta P}{\delta T}\right)_V$$

Here δQ denotes the quantity of heat absorbed by the system at constant temperature used in changing the volume. We know that heat absorbed at constant temperature is equal to the latent heat of the system. If L is the quantity of heat necessary to change unit mass of substance from one state to another, and V_1 and V_2 are the corresponding specific volumes of the substance, then

$$\left(\frac{\delta Q}{\delta V}\right)_T = \frac{L}{(V_2 - V_1)}$$

So that

$$\frac{L}{(V_2 - V_1)} = T \left(\frac{\delta P}{\delta T}\right)_V$$

or

$$\left(\frac{\delta P}{\delta T}\right)_V = \frac{L}{T(V_2 - V_1)}$$

This is Clausius Clapeyron latent heat equation.

(ii) Prove the thermodynamic relation $\left(\frac{\delta Q}{\delta P}\right)_T = -T \left(\frac{\delta V}{\delta T}\right)_P$

where the symbols have their usual meaning.

Or

Establish the following thermodynamical relation

$$\left(\frac{\delta Q}{\delta P}\right)_T = -TV\alpha$$

where α is the coefficient of volume expansion.

Proof. For answer this problem start exactly as we have obtained equation for general expression of Maxwell's thermodynamic relation *i.e.*,

$$\left(\frac{\delta T}{\delta y}\right)_x \left(\frac{\delta S}{\delta x}\right)_y - \left(\frac{\delta P}{\delta y}\right)_x \left(\frac{\delta V}{\delta x}\right)_y = \left(\frac{\delta T}{\delta x}\right)_y \left(\frac{\delta S}{\delta y}\right)_x - \left(\frac{\delta P}{\delta x}\right)_y \left(\frac{\delta V}{\delta y}\right)_x$$

Let us put $x = T$ and $y = P$ then

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

and

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

Substituting these values in the above expression

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P$$

Multiplying both sides by T , and putting

$$T\delta S = \delta Q$$

we get

$$\left(\frac{\delta Q}{\delta P}\right)_T = -T \left(\frac{\delta V}{\delta T}\right)_P \quad \dots(1)$$

This is required relation.

Now $\left(\frac{\delta V}{\delta T}\right)_P$ can be expressed in terms of the coefficient of volume expansion. The coefficient of volume expansion α is defined as in the increase in volume per unit volume per unit increase in temperature at constant pressure *i.e.*, expressed by $\frac{1}{V} \left(\frac{\delta V}{\delta T}\right)_P$.

Hence, $\frac{1}{V} \left(\frac{\delta V}{\delta T}\right)_P = \alpha$,

or

$$\left(\frac{\delta V}{\delta T}\right)_P = V\alpha \quad \dots(2)$$

From equations (1) and (2), we have

$$\left(\frac{\delta Q}{\delta P}\right)_P = -TV\alpha$$

Case (i) : When α is positive (i.e., body expands on heating), the left hand side $\left(\frac{\delta Q}{\delta P}\right)_T$ will be negative. This means that with increase of pressure under constant temperature condition, heat must be withdrawn from the body and if heat is not removed, it will cause a rise in its temperature. In other words, the increase in pressure will heat the body i.e., it expands on heating.

Case (ii) : When α is negative, (i.e., body contracts on heating), the left hand side $\left(\frac{\delta Q}{\delta P}\right)_T$ will be positive. It means that heat must be added to the body when the pressure is increased, if the temperature is to remain constant. In other words, the increase in pressure will cool a body which contracts on heating.

(iii) Prove that the ratio of adiabatic and isothermal elasticities for any substance is equal to $\left(\frac{C_p}{C_v}\right)$

Proof. The Maxwell's four thermodynamic relations for a homogeneous body are

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V \quad \dots(1)$$

$$\left(\frac{\delta S}{\delta P}\right)_T = -\left(\frac{\delta V}{\delta T}\right)_P \quad \dots(2)$$

$$\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V \quad \dots(3)$$

$$\left(\frac{\delta T}{\delta P}\right)_S = \left(\frac{\delta V}{\delta S}\right)_P \quad \dots(4)$$

If E_T and E_S are the isothermal and adiabatic elasticities of a substance and C_p and C_v its specific heat at constant pressure and constant volume, then we have to prove thermodynamically that

$$\frac{E_S}{E_T} = \frac{C_p}{C_v}$$

Let dQ represents the quantity of heat subject to unit mass of a substance under constant pressure and constant volume, resulting in a change in temperature dT , then

$$C_p = \left(\frac{dQ}{dT}\right)_P = T \left(\frac{\delta S}{\delta T}\right)_P$$

$$C_v = \left(\frac{dQ}{dT}\right)_V = T \left(\frac{\delta S}{\delta T}\right)_V$$

$$\frac{C_p}{C_v} = \frac{(\delta S/\delta T)_P}{(\delta S/\delta T)_V} \quad \dots(1)$$

Now the coefficient of elasticity E is defined by the expression

$$E = -\frac{dP}{\left(\frac{dV}{V}\right)}$$

Hence isothermal elasticity is

$$E_T = -V \left(\frac{\delta P}{\delta V}\right)_T$$

and adiabatic elasticity is

$$E_S = -V \left(\frac{\delta P}{\delta V}\right)_S$$

(as during adiabatic change entropy S remains constant)

Thus,

$$\frac{E_S}{E_T} = \frac{(\delta P/\delta V)_S}{(\delta P/\delta V)_T}$$

$$= \frac{\left(\frac{\delta P}{\delta T}\right)_S \left(\frac{\delta T}{\delta V}\right)_S}{\left(\frac{\delta P}{\delta S}\right)_T \left(\frac{\delta S}{\delta V}\right)_T} \quad \dots(2)$$

From Maxwell's Fourth relation $\left(\frac{\delta P}{\delta T}\right)_S = \left(\frac{\delta S}{\delta V}\right)_P$

Maxwell's third relation $\left(\frac{\delta T}{\delta V}\right)_S = -\left(\frac{\delta P}{\delta S}\right)_V$

Maxwell's second relation $\left(\frac{\delta P}{\delta S}\right)_T = -\left(\frac{\delta T}{\delta V}\right)_P$

and Maxwell's first relation $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$

Substituting these values in equation (2), we have

$$\frac{E_S}{E_T} = \frac{\left(\frac{\delta S}{\delta V}\right)_P \times -\left(\frac{\delta P}{\delta S}\right)_V}{-\left(\frac{\delta T}{\delta V}\right)_P \times \left(\frac{\delta P}{\delta T}\right)_V}$$

$$\frac{E_S}{E_T} = \frac{\left(\frac{\delta S}{\delta T}\right)_P}{\left(\frac{\delta S}{\delta T}\right)_V} \quad \dots(3)$$

Comparing equations (1) and (3), we get

$$\frac{E_S}{E_T} = \frac{C_P}{C_V}$$

(iv) Prove that $C_P - C_V = TE\alpha^2 V$

Proof. The molecular specific heat at constant pressure and at constant volume are defined

as

$$C_P = \left(\frac{\delta Q}{\delta T}\right)_P \quad \text{and} \quad C_V = \left(\frac{\delta Q}{\delta T}\right)_V$$

\(\therefore\)

$$C_P - C_V = \left(\frac{\delta Q}{\delta T}\right)_P - \left(\frac{\delta Q}{\delta T}\right)_V$$

$$= T \left(\frac{\delta S}{\delta T}\right)_P - T \left(\frac{\delta S}{\delta T}\right)_V \quad \text{as } (\delta Q = T\delta S) \quad \dots(4)$$

Considering the entropy S as a function of T and V , we can express it as

$$dS = \left(\frac{\delta S}{\delta T}\right)_V dT + \left(\frac{\delta S}{\delta V}\right)_T dV$$

or

$$\left(\frac{\delta S}{\delta T}\right)_P = \left(\frac{\delta S}{\delta T}\right)_V + \left(\frac{\delta S}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_P$$

Multiplying by T , we get

$$T \left(\frac{\delta S}{\delta T}\right)_P - T \left(\frac{\delta S}{\delta T}\right)_V = T \left(\frac{\delta S}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_P$$

Because $\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$ by Maxwell's first relation

$$T \left(\frac{\delta S}{\delta T}\right)_P - T \left(\frac{\delta S}{\delta T}\right)_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P$$

$$C_P - C_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P \quad \dots(5)$$

Again, considering P as a function of T and V

$$dP = \left(\frac{\delta P}{\delta T}\right)_V dT + \left(\frac{\delta P}{\delta V}\right)_T dV$$

If the change takes place under constant pressure, $dP = 0$. Then

$$\begin{aligned} \left(\frac{\delta P}{\delta T}\right)_V dT &= -\left(\frac{\delta P}{\delta V}\right)_T dV \\ \left(\frac{\delta P}{\delta T}\right)_V &= -\left(\frac{\delta P}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_P \end{aligned}$$

Putting the value of $\left(\frac{\delta P}{\delta T}\right)_V$ in equation (5), we have

$$\begin{aligned} C_p - C_v &= T \left(\frac{\delta P}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_P^2 \\ &= -\frac{T}{V} \left(\frac{\delta P}{\delta V/V}\right)_T V^2 \left(\frac{\delta V/V}{\delta T}\right)_P^2 \\ &= -T \left(\frac{\delta P}{\delta V/V}\right)_T \left(\frac{\delta V/V}{\delta T}\right)_P^2 V \end{aligned}$$

But $\left(-\frac{\delta P}{\delta V/V}\right)_T = E$ (Bulk modulus at constant temperature)

and $\left(\frac{dV/V}{\delta T}\right)_P = \alpha$ (coefficient of volume expansion.)

Therefore, $C_p - C_v = TE\alpha^2 V$

(v) Prove that

$$C_p - C_v = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P$$

the symbols have their usual meaning.

Hence prove that for a perfect gas $C_p - C_v = R$ and for a van der Waal's gas,

$$C_p - C_v = R \left(1 + \frac{2a}{RTV}\right)$$

Proof. For the thermodynamical relation

$$C_p - C_v = T \left\{ \frac{\delta P}{\delta T} \right\}_V \left\{ \frac{\delta V}{\delta T} \right\}_P \quad [\text{See Q. 5. eqn (5)}]$$

(i) **Perfect gas.** We know that in case of perfect gas $PV = RT$

$$\left(\frac{\delta P}{\delta T}\right)_V = \frac{R}{V} \quad \text{and} \quad \left(\frac{\delta V}{\delta T}\right)_P = \frac{R}{P}$$

Hence, $C_p - C_v = \frac{R^2 T}{pV}$, using the relation

But $PV = RT$,

$$C_p - C_v = \frac{R^2 T}{RT} = R$$

$$C_p - C_v = R$$

(ii) **van der Waal's gas.** For van der Waal's gas, we have

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

where a and b are constants. The equation may be written as

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

Differentiating it with respect to T at constant volume,

$$\left(\frac{\delta P}{\delta T}\right)_V = \frac{R}{(V-b)}$$

and also with respect to T at constant pressure

$$0 - \frac{2a}{V^3} \left(\frac{\delta V}{\delta T}\right)_P = -\frac{RT}{(V-b)^2} \left(\frac{\delta V}{\delta T}\right)_P + \frac{R}{V-b}$$

$$\left(\frac{\delta V}{\delta T}\right)_P \left(\frac{RT}{(V-b)^2} - \frac{2a}{V^3}\right) = \frac{R}{V-b}$$

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{\frac{R}{V-b}}{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}}$$

Putting the value of $\left(\frac{\delta P}{\delta T}\right)_V$ and $\left(\frac{\delta V}{\delta T}\right)_P$ in the relation

$$C_p - C_v = T \left\{ \frac{\delta P}{\delta T} \right\}_V \left\{ \frac{\delta V}{\delta T} \right\}_P, \text{ we have}$$

$$C_p - C_v = \frac{T \frac{R}{(V-b)} \frac{R}{(V-b)}}{\frac{RT}{(V-b)^2} - \frac{2a}{V^3}} = \frac{R}{1 - \frac{2a}{V^3} \cdot \frac{(V-b)^2}{RT}}$$

Since $b \ll V$, we may replace $(V-b)$ by V in the second power to get,

$$C_p - C_v = \frac{R}{1 - \frac{2a}{V^3} \cdot \frac{V^2}{RT}}$$

$$= R \left[1 - \frac{2V}{RTV} \right]^{-1}$$

Expanding by binomial theorem, we have

$$C_p - C_v = R \left(1 + \frac{2a}{RTV} \right)$$

(vi) Establish the relation

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

Proof. The molecular specific heat at constant pressure and at constant volume are defined as

$$C_p = \left(\frac{\delta Q}{\delta T} \right)_P \text{ and } C_v = \left(\frac{\delta Q}{\delta T} \right)_V$$

$$\therefore C_p - C_v = \left(\frac{\delta Q}{\delta T} \right)_P - \left(\frac{\delta Q}{\delta T} \right)_V$$

$$= T \left(\frac{\delta S}{\delta T} \right)_P - T \left(\frac{\delta S}{\delta T} \right)_V \quad [\because \delta Q = TdS] \quad \dots(1)$$

Let entropy S is a function of T and V then, we have

$$dS = \left(\frac{\delta S}{\delta T} \right)_V dT + \left(\frac{\delta S}{\delta V} \right)_T dV$$

or

$$\left(\frac{\delta S}{\delta T} \right)_P = \left(\frac{\delta S}{\delta T} \right)_V + \left(\frac{\delta S}{\delta V} \right)_T \left(\frac{\delta V}{\delta T} \right)_P$$

Multiplying by T , we get

$$T \left(\frac{\delta S}{\delta T} \right)_P - T \left(\frac{\delta S}{\delta T} \right)_V = T \left(\frac{\delta S}{\delta V} \right)_T \left(\frac{\delta V}{\delta T} \right)_P$$

From Maxwell's first relation,

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

$$\therefore T \left(\frac{\delta S}{\delta T}\right)_P - T \left(\frac{\delta S}{\delta T}\right)_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P$$

$$\therefore C_P - C_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P \quad \dots(2)$$

We know

$$dQ = dU + PdV$$

$$\left(\frac{\delta Q}{\delta V}\right)_T = \left(\frac{\delta U}{\delta V}\right)_T + P \quad \dots(3)$$

From Maxwell's first relation,

$$\left(\frac{\delta S}{\delta V}\right)_T = T \left(\frac{\delta P}{\delta T}\right)_V$$

and multiplying by T , we get

$$T \left(\frac{\delta S}{\delta V}\right)_T = T \left(\frac{\delta P}{\delta T}\right)_V$$

$$\left(\frac{\delta Q}{\delta V}\right)_T = T \left(\frac{\delta P}{\delta T}\right)_V \quad \dots(4)$$

From equations (3) and (4), we get

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

Putting in equation (2), we get

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

This is the desired result.

(vii) Prove the relations

$$TdS = C_P dT - T \left(\frac{\delta V}{\delta T}\right)_P dP$$

Proof. We have, $C_P - C_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P \quad \dots(1)$

and

$$C_P = \left(\frac{\delta Q}{\delta T}\right)_P \text{ and } C_V = \left(\frac{\delta Q}{\delta T}\right)_V$$

Putting the value of C_V in equation (1), we get

$$C_P - \left(\frac{\delta Q}{\delta T}\right)_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P$$

$$C_P dT - dQ = T dP \left(\frac{\delta V}{\delta T}\right)_P$$

$$dQ = C_P dT - T \left(\frac{\delta V}{\delta T}\right)_P dP$$

$$TdS = C_P dT - T \left(\frac{\delta V}{\delta T}\right)_P dP$$

$$[\because dQ = TdS]$$

This is the required result.

(viii) Prove the relation :

$$TdS = C_V dT + T \left(\frac{\delta P}{\delta T}\right)_V dV$$

Proof. We have,

$$C_P - C_V = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_P \quad \dots(1)$$

Putting the value of C_p in equation (1), we get

$$\left(\frac{\delta Q}{\delta T}\right)_p - C_p = T \left(\frac{\delta P}{\delta T}\right)_V \left(\frac{\delta V}{\delta T}\right)_p$$

$$dQ - C_p dT = T \left(\frac{\delta P}{\delta T}\right)_V dV$$

$$dQ = C_p dT + T \left(\frac{\delta P}{\delta T}\right)_V dV$$

$$TdS = C_p dT + T \left(\frac{\delta P}{\delta T}\right)_V dV$$

This is the desired result.

• 4.4. JOULE-THOMSON EFFECT

Joule and Thomson experimentally shown that when a gas under constant pressure is passed through a **porous plug**, to a region of lower constant pressure, then its temperature changes. This phenomenon is known as "Joule-Thomson or Joule-Kelvin effect."

From this experiment following results are obtained :

(i) The change in temperature is directly proportional to the pressure difference on both sides of the porous plug.

(ii) All the gases, when passed through the porous plug, suffer a change in temperature.

(iii) The fall in temperature per unit atmospheric pressure difference decreases as the initial temperature of the gas is raised, becomes zero at a particular temperature and above this temperature heating is produced. The temperature at which the behaviour of gas changes, is known as **temperature of inversion**. It is denoted by T_i .

(iv) All the gases (except H_2 and He) show cooling effect at ordinary temperature, while H_2 and He show heating effect.

Explanation of Results : Let P_1 , V_1 and T_1 be the pressure, volume and temperature, respectively of the gas of unit mass on high pressure side before passing through the porous plug and P_2 , V_2 and T_2 after passing through the porous plug. Since there is no heat-exchange between the gas and its surroundings, this work must come from the internal energy of the gas. Thus, if U_1 and U_2 be the internal energies of the gas before and after passing through the porous plug, then from the first law of thermodynamics

$$U_1 - U_2 = P_2 V_2 - P_1 V_1$$

or

$$U_1 + P_1 V_1 = U_2 + P_2 V_2$$

∴

$$U + PV = \text{constant}$$

The total heat function ($U + PV$) remains constant during the process, is called enthalpy (H) of the gas. Thus,

$$dH = d(U + PV) = 0$$

$$dU + PdV + VdP = 0 \quad \dots(1)$$

First law of thermodynamics is

$$dU + PdV = dQ$$

and second law of thermodynamics is

$$dQ = TdS$$

So equation (1), reduces to

$$TdS + VdP = 0 \quad \dots(2)$$

Let S be a function of two independent variables P and T . Since dS is a perfect differential, so we have

$$dS = \left(\frac{\delta S}{\delta T}\right)_P dT + \left(\frac{\delta S}{\delta P}\right)_T dP$$

Putting in equation (2), we get

$$T \left(\frac{\delta S}{\delta T}\right)_P dT + T \left(\frac{\delta S}{\delta P}\right)_T dP + VdP = 0 \quad \dots(3)$$

$$C_p = \left(\frac{\delta Q}{\delta P} \right)_p = T \left(\frac{\delta S}{\delta T} \right)_p \text{ and } \left(\frac{\delta S}{\delta P} \right)_p = - \left(\frac{\delta V}{\delta T} \right)_p \quad (\text{Maxwell's IVth relation})$$

Therefore, equation (3) becomes

$$C_p dT - T \left(\frac{\delta V}{\delta T} \right)_p dP + V dP = 0$$

$$C_p dT = \left[T \left(\frac{\delta V}{\delta T} \right)_p - V \right] dP$$

$$\left(\frac{dT}{dP} \right)_p = \frac{T \left(\frac{\delta V}{\delta T} \right)_p - V}{C_p}$$

This is the required expression for the change in temperature (dT) while the pressure difference dP remains constant.

We know heat given at constant pressure is known as enthalpy H . Therefore we can write $\frac{dT}{dP}$ as $\left(\frac{\delta T}{\delta P} \right)_H$ which is known as Joule-Thomson coefficient μ . Thus

$$\mu = \left(\frac{\delta T}{\delta P} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\delta V}{\delta T} \right)_p - V \right] \quad \dots(3)$$

In integrated form above expression may also be written as

$$\Delta T = \frac{1}{C_p} \int_{P_1}^{P_2} \left[T \left(\frac{\delta V}{\delta T} \right)_p - V \right] dP \quad \dots(4)$$

Now we have to apply this relation for different gases.

(1) **Perfect gas** : For 1 mole of a perfect gas, we have $PV = RT$

$$\left(\frac{\delta V}{\delta T} \right)_p = \frac{R}{P}$$

$$T \left(\frac{\delta V}{\delta T} \right)_p = \frac{RT}{P} = V \quad [\because PV = RT]$$

$$T \left(\frac{\delta V}{\delta T} \right)_p - V = 0$$

So, by equations (3) and (4), we get

$$\mu = \Delta T = 0$$

This means that, the **Joule-Thomson effect for a perfect gas is zero.**

(2) **van der Waal's gas equation** : van der Waal's gas equation is given by

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

Differentiating it with respect to T , taking P as constant, we get

$$\left(P + \frac{a}{V^2} \right) \left(\frac{\delta V}{\delta T} \right)_p - \frac{2a}{V^3} \left(\frac{\delta V}{\delta T} \right)_p (V - b) = R$$

$$\left(\frac{\delta V}{\delta T} \right)_p = \frac{R}{\left(P + \frac{a}{V^2} \right) - \frac{2a(V-b)}{V^3}}$$

$$\left(\frac{\delta V}{\delta T} \right)_p = \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^3}(V-b)} = \frac{R(V-b)}{RT - \frac{2a}{V^3}(V-b)^2}$$

Since $b \ll V$, so we can neglect it in the square term $(V-b)^2$, thus

$$T \left(\frac{\delta V}{\delta T} \right)_p = \frac{RT(V-b)}{RT - \frac{2a}{V}} = \frac{V-b}{1 - \frac{2a}{VRT}}$$

$$\begin{aligned}
 &= (V-b) \left(1 - \frac{2a}{VRT} \right)^{-1} \\
 &= (V-b) \left[1 + \frac{2a}{VRT} \right] \\
 &= V - b + \frac{2a}{RT} - \frac{2ab}{VRT}
 \end{aligned}$$

On neglecting $\frac{2ab}{VRT}$, we get

$$T \left(\frac{\delta V}{\delta T} \right)_P - V = \frac{2a}{RT} - b$$

So by equations (3) and (4), we get

$$\mu = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$$

and

$$\Delta T = \frac{\frac{2a}{RT} - b}{C_p} (P_2 - P_1)$$

But $P_2 < P_1$, so

$$\Delta T = \frac{\left(\frac{2a}{RT} - b \right)}{C_p} (P_1 - P_2)$$

From this expression it is clear that :

- (i) If $\frac{2a}{RT} > b$, then ΔT will be negative *i.e.*, cooling is produced.
- (ii) If $\frac{2a}{RT} < b$ then ΔT will be positive, *i.e.*, heating is produced.

(iii) When $\frac{2a}{RT} = b$, we have $\Delta T = 0$, *i.e.*, there is no change in the temperature of the gas. This is called the 'temperature of inversion' T_i . At this temperature, the Joule-Thomson coefficient $\mu = 0$.

$$T_i = \frac{2a}{Rb} = \frac{27}{4} T_c = 2T_B$$

For most gases $T_i > T$ *i.e.*, temperature of inversion is greater than the ordinary temperature. Hence they show a cooling effect. In case of hydrogen and helium, the inversion temperatures are much below the ordinary temperature, hence they show heating effect at ordinary temperature.

Hence any gas below its temperature of inversion will show cooling effect after passing through porous plug.

• STUDENT ACTIVITY

1. Why the expression for Joule-Thomson cooling is zero for a perfect gas ?

2. Define the temperature of inversion.

• 4.5. THERMODYNAMIC FUNCTIONS

The thermodynamic variables P , V , T and S define the state of a thermodynamical system. From first and second law of thermodynamics, we have

$$dQ = dU + dW$$

$$dQ = dU + PdV$$

and $dQ = TdS$

On combining these two, we get

$$TdS = dU + PdV$$

$$dU = TdS - PdV \quad \dots(1)$$

If any two of these four variables are independent then the remaining variables can be calculated by using the above relations. For the full description of a thermodynamical phenomenon, certain other relations among these variables are required. These relations are known as 'thermodynamic functions' or 'thermodynamic potentials'. They are four in number.

(i) **Internal Energy or Intrinsic energy (U)**: Each matter is made up of molecules. These molecules are in constant rapid motion and exert the force of attraction on each other. Due to the rapid motion, they possess internal kinetic energy and due to the force of attraction they have internal potential energy. The sum of these two energies is called total *internal energy* of the system.

$$dU = dQ - dW$$

$$dQ = TdS, \quad dW = PdV$$

$$dU = TdS - PdV \quad \dots(1)$$

From equation (1), we have

$$dU = TdS - PdV \quad \dots(2)$$

Differentiating this partially with respect to V and S , we get

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad \text{and} \quad \left(\frac{\partial U}{\partial S}\right)_V = T \quad \dots(3)$$

Since dU is a perfect differential, so we can write

$$\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right) = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right) \quad \dots(4)$$

From equations (3) and (4), we get

$$\boxed{\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S}$$

This is the first thermodynamical relation.

(2) **Helmholtz Function (F)**: Thermodynamic potential at constant temperature is known as Helmholtz function or Helmholtz free energy.

Since U , T and S are perfect differentials therefore F is also perfect differential.

From equation (1), we have

$$dU = TdS - PdV$$

If the temperature of the system remains constant, then

$$d(TS) = TdS$$

Therefore, $dU = d(TS) - PdV$
 or $d(U - TS) = -PdV$
 or $dF = -PdV$
 where $F = U - TS$... (5)

The function $F = U - TS$ is called **Helmholtz function** or **Helmholtz free energy**. This function is also called work function.

From equation (4), we have

$$dF = dU - TdS - SdT$$

But

$$dU = TdS$$

∴

$$dF = TdS - PdV - TdS - SdT$$

$$dF = -PdV - SdT$$

Differentiating partially F with respect to T and V , we get

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$
 ... (6)

Since dF is a perfect differential, so we can write

$$\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)$$
 ... (7)

From equations (6) and (7), we get

$$\left[\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V\right]$$
 ... (8)

This is the second thermodynamic relation.

(3) Enthalpy or Heat Content (H) : Enthalpy is equal to the total heat of the system at constant pressure.

The enthalpy of the system is given the relation

$$H = U + PV$$
 ... (9)

Differentiating it, we get

$$\begin{aligned} dH &= dU + PdV + VdP \\ &= TdS - PdV + PdV + VdP \quad [\because dU = TdS - PdV] \\ &= TdS + VdP \end{aligned}$$
 ... (10)

Since the process is carried at constant pressure. Therefore

$$dH = TdS \quad [\because dP = 0]$$

or

$$dH = dQ \quad [\because TdS = dQ]$$

From this, it is clear that enthalpy is equivalent to heat given to the system at constant pressure.

From equation (10), we have

$$dH = TdS + VdP$$

Differentiating partially with respect to S and P , we get

$$\left. \begin{aligned} \left(\frac{\partial H}{\partial S}\right)_P &= T \\ \left(\frac{\partial H}{\partial P}\right)_S &= V \end{aligned} \right\}$$
 ... (11)

and

Since dH is a perfect differential, so

$$\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right)$$
 ... (12)

From equations (11) and (12), we get

$$\left[\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S\right]$$
 ... (13)

This is the third thermodynamic relation.

(4) Gibb's Potential (G) : Gibb's potential or free energy may be defined as "thermodynamic potential at constant volume. It is defined as

$$G = H - TS$$

From $dH = TdS + VdP$
 For isobaric process, $dP = 0$
 Therefore, $dH = TdS$
 $dH = d(TS)$

$$d(H - TS) = 0$$

$$dG = 0$$

where $G = H - TS$ is called Gibb's free energy.

$$G = U + PV - TS \quad \dots(14)$$

$$\begin{aligned} dG &= dU + PdV + VdP - TdS - SdT \\ &= (TdS - PdV) + PdV + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned} \quad \dots(15)$$

Differentiating partially G with respect to P and T , we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \dots(16)$$

Since dG is a perfect differential, so

$$\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right) \quad \dots(17)$$

From equations (16) and (17), we get

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

This is the fourth thermodynamic relation.

Significance : From above, it is clear that at constant temperature and constant pressure ($dT = 0, dP = 0$), $dG = 0$ and $G = \text{constant}$. That is, Gibb's free energy never increases.

Gibb's function (G) is also known as "Gibb's free energy" or "Thermodynamic potential at constant pressure."

4.6. ENTHALPHY

Enthalpy of a thermodynamic system is given by

$$H = U + PV$$

or $dH = dU + PdV + VdP$

$$= dQ + VdP \quad [\because dQ = dU + PdV]$$

For isentropic process, pressure remains constant. Therefore

$$dH = dQ \quad [\because dP = 0]$$

From this it is clear that the change in enthalpy during an isobaric process is equal to the heat transferred.

4.7. ISENTHALPIC CURVE

Isenthalpic curve is the locus of all points which gives the equilibrium state of the same enthalpy of a thermodynamic system. For a gas it can be drawn from porous plug experiment as follows :

(i) Choose some initial value of pressure P_1 and temperature T_1 , on the high pressure side of the plug.

(ii) Select a pressure, P_2 which is less than P_1 , on the other side of the porous plug. Measure temperature, T_2 of the gas on this side.

(iii) Select some other value of pressure P_2 and measure temperature T_2 . This is done for different values of P_2 and corresponding temperatures T_2 are measured.

A graph is plotted for various values of temperature and pressure (P_2, T_2). Since for throttling process, the initial and final enthalpies are same i.e., $\Delta H = 0$, therefore all (P_2, T_2)

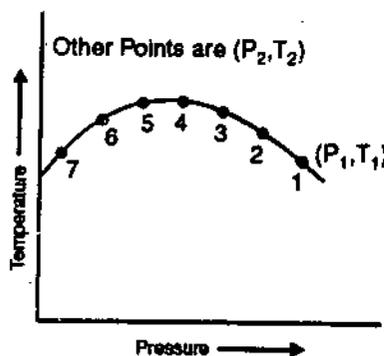


Fig. 3

points give the equilibrium state of a gas of constant mass and constant enthalpy. The curve formed by these points, is known as isenthalpic curve.

Similarly, other curves corresponding to different enthalpies can be obtained by different values of T_1 . For an ideal gas, we have

$$PV = RT$$

and enthalpy is

$$H = U + PV$$

$$\therefore H = U + RT$$

From this, it is clear that enthalpy remains constant because for isothermal process, temperature T and internal energy U remain constant.

Therefore, $H = \text{constant}$.

Hence an isothermal curve for an ideal gas is also isenthalpic.

• 4.8. GIBB'S HELMHOLTZ REACTION

Helmholtz free energy is given by

$$F = U - TS$$

$$\begin{aligned} \therefore dF &= dU - TdS - SdT \\ &= TdS' - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned} \quad \dots(1)$$

Gibb's free energy is given by

$$G = U + PV - TS'$$

$$\begin{aligned} \therefore dG &= dU + PdV + VdP - TdS - SdT \\ &= VdP - SdT \end{aligned} \quad \dots(2)$$

Consider two processes in which P and V remain constant.

(i) **Isobaric Process** : In this process pressure remains constant ($dP = 0$). Therefore from equation (2), we get

$$dG = -SdT$$

$$\text{or} \quad \left(\frac{\partial G}{\partial T} \right)_P = -S$$

$$\text{We know} \quad G = H - TS$$

$$\therefore \quad G = H + T \left(\frac{\partial G}{\partial T} \right)_P \quad \dots(3)$$

(ii) **Isochoric Process** : In this process volume remains constant, i.e., $dV = 0$, so by equation (1), we get

$$dF = -SdT$$

$$\text{or} \quad \left(\frac{\partial F}{\partial T} \right)_V = -S$$

$$\text{We have,} \quad F = U - TS$$

$$\therefore \quad F = U + T \left(\frac{\partial F}{\partial T} \right)_V$$

$$\text{or} \quad U = F - T \left(\frac{\partial F}{\partial T} \right)_V \quad \dots(4)$$

Equations (3) and (4) relate Gibbs free energy G with enthalpy H and Helmholtz free energy F with internal energy U . These relations are known as **Gibbs-Helmholtz relations**. Since these relations do not contain entropy S , therefore it can easily be applied to study the thermodynamics of isothermal changes in a system.

• STUDENT ACTIVITY

3. Explain enthalpy.

4. Define isenthalpic curve.

• 4.9. CLAUSIUS-CLAPEYRON EQUATION (FIRST LATENT HEAT EQUATION)

Clausius and Clapeyron deduced an equation which explains the effect of pressure on the boiling points of liquids and melting points of solids.

This equation is known as "Clausius-Clapeyron equation" or the "first latent heat equation".

Let us consider two isothermals $ABCD$ and $EFGH$ at temperatures T and $T + dT$ as shown in the fig. 4. Let at point D , the gas be in vapour state. When the pressure is increased, then the volume of the unsaturated vapour decreases. At point C , the vapour becomes **just** saturated. If the pressure is further increased, then the condensation of vapour starts and along CB the liquid and vapour phases of the substance exist together in equilibrium at temperature T . At point B , the substance is fully liquid and any further increase in pressure does not effect much the volume because liquids are almost **incompressible**. This is shown by the curve BA in the fig. 4. The another isothermal at temperature $T + dT$ represents the same general features. Thus, from the fig. 4 at point C and G , the vapour is just saturated and at points B and F the substance is totally liquid. From F and G draw adiabatics at M and N .

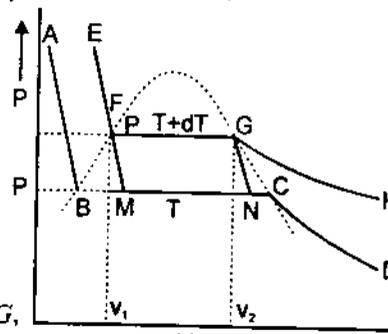


Fig. 4

Consider for Carnot cycle $FGNM$, the Carnot's engine contains one gm of the liquid in the state shown by the point F . Here the following processes take-place.

(i) A reversible isothermal expansion along FG . In this process, the liquid is converted into vapour. Due to this, the heat Q_1 is absorbed at temperature $T + dT$ which is equal to $(L + dL)$.

(ii) A reversible adiabatic expansion along GN .

(iii) A reversible isothermal compression along NM . In this process, the vapour converts into liquid and the heat Q_2 is given up at temperature T which is equal to L .

(iv) A reversible adiabatic compression along MF .

We know that for Carnot's cycle, the efficiency is

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

But

$$Q_1 = L + dL$$

$$Q_2 = L$$

$$T_1 = T + dT$$

and

$$T_2 = T$$

Therefore,

$$\frac{(L + dL) - L}{L + dL} = \frac{(T + dT) - T}{T + dT}$$

or

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

or

$$TdL + dLdT = LdT + dLdT$$

$$TdL = LdT$$

$$dL = \frac{L}{T} dT \quad \dots(1)$$

$$\begin{aligned} \text{Heat converted into work} &= Q_1 - Q_2 \\ &= (L + dL) - L \\ &= dL \end{aligned}$$

∴

$$Q_1 - Q_2 = dL \quad \dots(2)$$

From figure 4, the work done is equal to the area $FGNM$. Thus,

$$dL = FG \times \text{perpendicular distance} \\ \text{between } FG \text{ and } NM$$

or

$$dL = (V_2 - V_1) dP \quad \dots(3)$$

From equations (1) and (3), we get

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

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

This is known as Clausius-Clapeyron latent heat equation.

(i) **Effect of pressure on boiling point of liquids :** The substance at the point F is totally in the liquid state and along FG it exists partly in liquid and partly in vapour state. We know that the specific volume of a substance in the vapour state is much larger than in the liquid state, i.e., $V_2 > V_1$. Hence $(V_2 - V_1)$ is always positive and $\frac{dP}{dT}$ is also positive. This means that the boiling point of every liquid increases with increase in pressure.

(ii) **Effect of pressure on melting point of solids :** For those substances, which expand on melting, like wax and sulphur, $(V_2 - V_1)$ is positive. In this position $\frac{dP}{dT}$ is positive. Thus the melting point rises with increase in pressure.

For those substances like ice which contracts on melting, $(V_2 - V_1)$ is negative. In this position $\frac{dP}{dT}$ will be negative, i.e., the melting point decreases with increase in pressure.

• 4.10. CLAUSIUS' LATENT HEAT EQUATION (Second Latent Heat Equation)

Clausius deduced an equation which gives the variation of latent heat of a substance with temperature and connects it with the specific heat of the substance in the two states. It is given by

$$S_2 - S_1 = \frac{dL}{dT} - \frac{L}{T}$$

Let us consider two isothermals $ABCD$ and $EFGH$ at temperatures T and $T + dT$ as shown in the fig. 5. The parts AB and EF represent the liquid state and the parts BC and FG represent the saturated vapour in contact with liquid and the parts CD and GH indicate the unsaturated vapour state. The dotted curve represents the boundary separating the different regions.

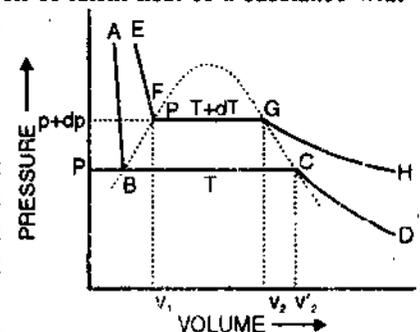


Fig. 5

Let S_1 and S_2 are the specific heats in liquid state and in saturated state, respectively. Here the following processes take place :

(i) During the passage of liquid from B to F , when its temperature increases by dT , then the heat absorbed by it is given by

$$= S_1 dT$$

(ii) Along FG , the substance changes from liquid to vapour. In this position, the heat absorbed is

$$= L + dL$$

(iii) Along the path GC , the temperature decreases by dT and the heat given by the vapour is

$$= S_2 dT$$

(iv) During the path CB , the heat given by the vapour at constant temperature is

$$= L$$

Net amount of heat used during the cycle $BFGCB$ is

$$\begin{aligned} &= S_1 dT + L + dL - S_2 dT - L \\ &= (S_1 - S_2) dT + dL \end{aligned} \quad \dots(1)$$

We know that the amount of heat used is equal to the work done which is given by the area $BFGCB$

$$\begin{aligned} &= FG \times dP \\ &= (V_2 - V_1) dP \end{aligned} \quad \dots(2)$$

From Clausius-Clapeyron's latent heat equation

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

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

Hence the amount of work done $= \frac{L}{T} dT \quad \dots(3)$

From equations (1) and (3), we get

$$(S_1 - S_2) dT + dL = \frac{L}{T} dT$$

$$S_1 - S_2 = \frac{L}{T} - \frac{dL}{dT}$$

or
$$S_2 - S_1 = \frac{dL}{dT} - \frac{L}{T}$$

This is the required expression. This equation is known as second latent heat equation.

Explanation of negative specific heat of saturated water vapour at 100°C : From the fig. 5, the substance at point G is in the saturated vapour state at temperature $(T + dT)$ and at point C , it is again in the saturated vapour state but at the different temperatures T . The dotted passing through the points G and C is known as curve of saturation. From the fig. 5, it is clear that the volume V_2' at point C is greater than the volume V_2 at point G . During the path CG , the volume is decreased, i.e., the vapour is compressed. Due to this, heat is produced which increases the temperature of vapour. In this position, the temperature of the vapour increases from T to $T + dT$ and hence some heat is withdrawn from vapour to maintain its temperature $(T + dT)$. This means that the specific heat of saturated water vapour is negative.

Physical Significances : The negative heat implies that when saturated water vapour is compressed adiabatically then certain amount of heat produced in this process which make it super-heated or it becomes saturated and behave as a perfect gas. During adiabatic expansion, it is super cooled which is not a stable process, i.e., vapour condenses partly.

Application : The negative specific heat of saturated vapour is used in observing the tracks of charged particles passing through a Wilson cloud chamber.

• SUMMARY

- The temperature at which the behaviour of gas changes, is known as temperature of inversion.
- For most gases $t_i > T$, i.e., temperature of inversion is greater than ordinary temperature.
- Thermodynamic potential at constant temperature is known as Helmholtz free energy.

- The function $F = U - TS$ is called Helmholtz function.
- Enthalpy is equal to the total heat of the system at constant pressure.
- Gibb's potential is equal to thermodynamic potential at constant volume.
- The boiling point of every liquid increases with increase in pressure.

• TEST YOURSELF

1. Explain the perfect differentials with examples.
2. Derive Maxwell's four thermodynamic relations.
3. Prove the thermodynamic relation

$$\left(\frac{\delta S}{\delta V}\right)_T = \left(\frac{\delta P}{\delta T}\right)_V$$

and hence prove the Clausius-Clapeyron equation

$$\frac{\delta P}{\delta T} = \frac{L}{T(V_2 - V_1)}$$

4. Prove that

$$C_P - C_V = TE\alpha^2 V$$

where C_P and C_V are the molecular specific heats at constant pressure and constant volume respectively. E is the Bulk modulus of elasticity, α is the coefficient of volume expansion and V is the volume.

5. Deduce the expression for Joule-Thomson cooling from thermodynamics.
6. Explain four thermodynamical potentials U , F , H and G . Deduce Maxwell's thermodynamical relations from them.
7. Derive first latent heat equation of Clausius-Clapeyron *i.e.*,

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

8. Prove that

$$S_2 - S_1 = \frac{dL}{dT} - \frac{L}{T}$$

where, S_1 and S_2 are the specific heats of liquid and saturated vapour and L is the latent heat of vaporisation.

9. Maxwell's important thermodynamical relations are :

(a) Two (b) Four (c) Eight (d) None of these

10. The internal energy of an ideal gas is independent of its volume at constant temperature. This law is known as :

(a) Newton's law (b) Stefan's law
(c) Joule's law (d) van der Waal's law

11. The quantity $U + pV$ is known as :

(a) Entropy (b) Total energy (c) Enthalpy (d) None of these

12. Joule Thomson effect for a perfect gas is :

(a) Infinity (b) Zero (c) Indeterminate (d) None of these

13. Clausius-Clapeyron heat equation is :

(a) $\frac{dp}{dT} = \frac{L}{T(p_2 - p_1)}$ (b) $\frac{dp}{dT} = \frac{L}{p(V_2 - V_1)}$
(c) $\frac{dp}{dT} = \frac{L}{V(p_2 - p_1)}$ (d) $\frac{dp}{dV} = \frac{L}{T(V_2 - V_1)}$

14. Enthalpy of a system can be written as :

(a) $H = U + Q$ (b) $H = Q + pV$
(c) $H = U + pV$ (d) None of these

15. In a porous plug process, the initial and final enthalpies of the system are :

(a) Equal (b) Zero (c) Different (d) None of these

ANSWERS

9. (b) 10. (c) 11. (c) 12. (b) 13. (a) 14. (c) 15. (a)



UNIT

5

RADIATION

STRUCTURE

- Bartoli's Proof of the Existence of Pressure of Radiation
- Black Body and Black-Body Radiation
- Emissive Power
 - Student Activity
- Stefan's Law
- Stefan's-Boltzmann's Law
- Spectrum of Black Body Radiation
- Planck's Mechanism of Emission and Absorption of Radiation
- Solar Constant
 - Student Activity
- Dulong and Petit Law
- Einstein's Quantum Theory of Specific Heat
- Debye's Theory of Specific Heat of Solids
 - Summary
 - Test Yourself

LEARNING OBJECTIVES

After going this unit you will learn :

- Realisation of black body in practice.
- Fery's black body and Wien's black body.
- Absorptive power and Kirchhoff's law with importance.
- Thermodynamic proof and experimental verification of Stefan's law.
- The determination of Stefan's constant σ .
- Explanation of classical theory : Wien's law and Planck's law.
- Average energy of Planck's oscillator.
- Rayleigh-Jeans Formula.
- Determination of solar constant and temperature of sun.
- Deduction of Dulong and Petit's law from kinetic theory.
- Variation of specific heat with temperature.

5.1. BARTOLI'S PROOF OF THE EXISTENCE OF PRESSURE OF RADIATION

Maxwell, on the basis of electromagnetic theory, showed that light exerts a pressure on the surface on which it is incident. A thermodynamic proof of the existence of radiation pressure is as follows :

Let us consider a cylinder whose walls are perfectly reflecting and its both ends C and D are perfectly conducting. Let T_1 and T_2 be constant temperatures of D and C , respectively, such that $T_1 > T_2$.

It consists of two perfectly reflecting screens A and B . V is the valve in the screen B . When the valve V is open, the space AC is filled with radiation which is in equilibrium with black body C at temperature T_2 while the space AD is filled with radiation which is in equilibrium with black body D at temperature T_1 .

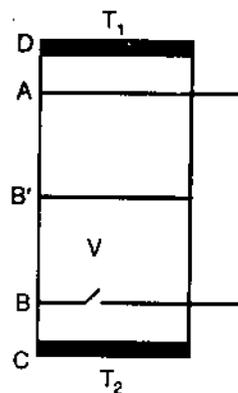


Fig. 1

Now the valve V is closed and the screen B is pushed up to the position B' . In this position the radiation is compressed with in the space AB' and its density in AB' becomes greater than that in AD . When the screen A is withdrawn, then the space $B'D$ will have much more radiation than necessary for equilibrium with the black body D at temperature T_1 . In this position the excess radiation will be absorbed by D . Hence, the heat is transferred from a colder body C to hotter body D . This shows that some work is done in pushing the screen B upward or we can say that B has been pushed upwards against a pressure. Thus, radiation exerts pressure. Here we shall take up two cases :

(i) **When light (photon) is incident normally on the surface :** Let a photon of energy $h\nu$ moving with the velocity of light. In this position the energy of photon is given by

$$E' = mc^2 = h\nu$$

or

$$m = \frac{h\nu}{c^2}$$

so that momentum of photon will be

$$= \text{mass} \times \text{velocity}$$

$$= \frac{h\nu}{c^2} \cdot c = \frac{h\nu}{c}$$

$$= \frac{E'}{c}$$

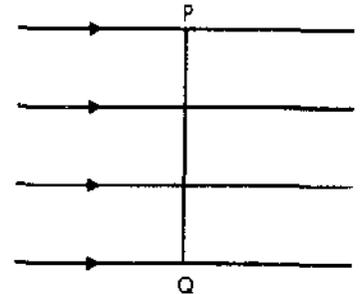


Fig. 1

Now the momentum incident on the surface PQ per unit area per sec. is given by

$$p = \Sigma \frac{E'}{c} = \frac{E}{c} \quad \dots(1)$$

where E is the total energy incident on the surface per unit area per sec.

If u is the energy density, then the total energy passing through any surface of surface area s is normal to the radiation per second

$$= u \times sc$$

Therefore, the energy radiations per unit area per second

$$E = \frac{usc}{s} = uc \quad \dots(2)$$

From equations (1) and (2), we get

$$p = u$$

Thus, the pressure of radiation for normal incidence is equal to the energy density.

(ii) **When the radiation is diffuse (i.e., photons move in all possible directions) :** Let the beam of radiation is incident at an angle θ to the surface OR as shown in the fig. 3. Draw a normal RQ to the beam so that energy incident on RQ per second

$$= Es = ucs$$

where s is the surface area of RQ and $s = s' \cos \theta$
where s' is the surface area of surface OR .

The total energy passing through the surface RQ is equal to the energy incident on the surface OR per second. Therefore energy incident on the plane OB per unit area per second

$$= \frac{ucs}{s} = \frac{ucs' \cos \theta}{s'}$$

$$= uc \cos \theta$$

The momentum incident on the surface OB per unit area per second

$$= \frac{uc \cos \theta}{c} = u \cos \theta$$

The component of this momentum in the direction normal to OR is

$$= (u \cos \theta) \cos \theta = u \cos^2 \theta$$

If this radiation is absorbed, then the pressure on the surface is

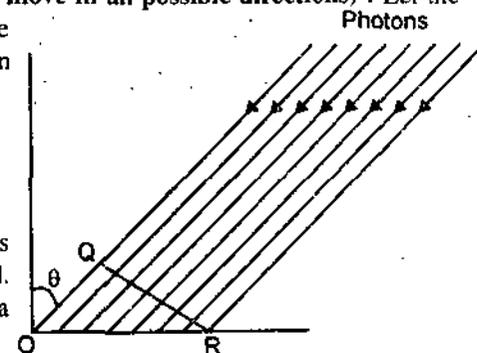


Fig. 3

$$P = u \cos^2 \theta$$

In the case of diffuse radiation, the radiation is incident from all possible directions with equal probability. Therefore, pressure of diffuse radiation

$$= u \overline{\cos^2 \theta}$$

where $\overline{\cos^2 \theta}$ represents averaged $\cos^2 \theta$ over all directions.

Consider the radiation to be equivalent to a large number of beams of equal intensity (say N), distributed uniformly over all directions.

In order to calculate $u \cos^2 \theta$, draw a hemisphere of radius r with centre T of the element OR . Consider a small element of this hemisphere. It will be a ring.

$$\begin{aligned} \text{Area of this ring} &= 2\pi r \sin \theta, r d\theta \\ &= 2\pi r^2 \sin \theta d\theta \end{aligned}$$

If N are the number of beams, then the number of beams passing through the area of the ring.

$$\begin{aligned} dN &= \frac{2\pi r^2 \sin \theta d\theta}{2\pi r^2} N \\ &= N \sin \theta d\theta \end{aligned}$$

Fraction of beams incident between angles θ and $\theta + d\theta$

$$= \frac{dN}{N} = \sin \theta d\theta$$

The pressure due to radiation is

$$\begin{aligned} P &= \frac{dN}{N} \times u \cos^2 \theta \\ &= \sin \theta d\theta u \cos^2 \theta \\ &= u \cos^2 \theta \sin \theta d\theta \end{aligned}$$

For all possible rings, the pressure is

$$P = \int_0^{\pi/2} u \cos^2 \theta \sin \theta d\theta$$

or
$$P = u \int_0^{\pi/2} \cos^2 \theta \sin \theta d\theta$$

Let
$$x = \cos \theta$$

$$dx = -\sin \theta d\theta$$

Therefore,

$$\begin{aligned} P &= u \int_1^0 x^2 (-dx) = u \int_0^1 x^2 dx \\ &= u \left[\frac{x^3}{3} \right]_0^1 \\ &= \frac{u}{3} \end{aligned}$$

Thus, the pressure due to diffuse radiation is one third of the energy density.

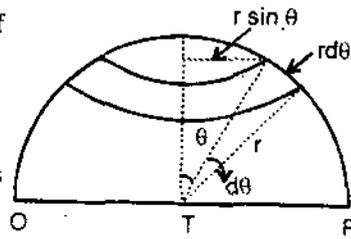


Fig. 4

• 5.2. BLACK BODY AND BLACK-BODY RADIATION

The body which absorbs all the heat radiations incident on it, whatever be the wavelength, is known as perfectly black body.

When a radiation is incident on a black body, then no part of it is reflected or transmitted for any wavelength. This means that no radiation of any colour will reach our eyes and hence the body will appear black. Thus it neither reflects nor transmits any of the incident radiations and appears black whatever be the incident radiation.

According to Kirchhoff, **black body has the property of allowing all incident rays to enter itself without reflection and not allowing them to leave again.** It is found that inside a black body,

the nature of radiation is independent of the shape, size and material of the body. This radiation is called black body radiation. The radiation emitted by a black body is the full radiation which consists of all possible wavelengths.

Realisation of Black Body in Practice : In practice no substance possesses strictly the properties of a black body. Lamp-black and the platinum black are the nearest approach to a black body. Thus black body is only an ideal conception. The most important characteristic of a black body is that when heated up to high temperature then it emits radiations of all wavelengths and hence, it consists of a continuous spectrum. It is a perfect absorber as well as perfect emitter.

There are two devices which are used as perfectly black bodies by different physicists.

(a) Fery's Black Body : It is based on the principle that radiation inside an isothermal enclosure is a perfectly black body radiation. Isothermal enclosure means, an enclosure having constant uniform temperature.

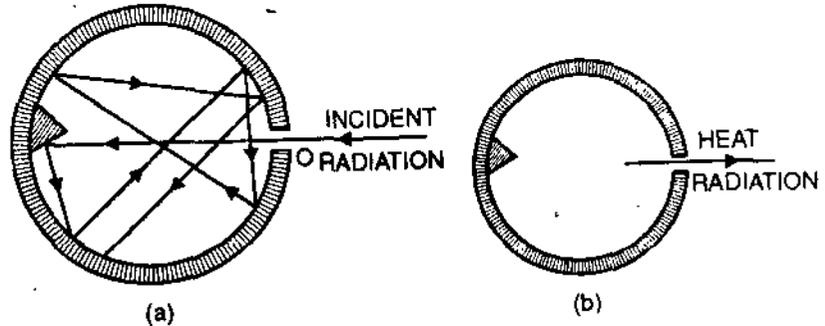


Fig. 5

It consists of a hollow copper sphere blackened inside with a small fine hole O in the surface. The space between the walls is evacuated so that no heat is lost through conduction. To avoid direct reflection of radiations from the inner surface, a pointed projection is made in front of the hole as shown in fig. 5.

When the radiations enter the sphere through the hole O , then they suffer multiple reflections on the inner walls and are completely absorbed finally.

(b) Wien's Black Body : This is the commonly used source of black body radiation. It consists of a long hollow metallic cylinder C blackened inside with heating coils around it.

It is heated by an electrical current flowing in coil wound around it. The radiation passes through a number of limiting diaphragms and comes out through a narrow hole O in the wall of the tube. The temperature is measured by a thermo couple T .

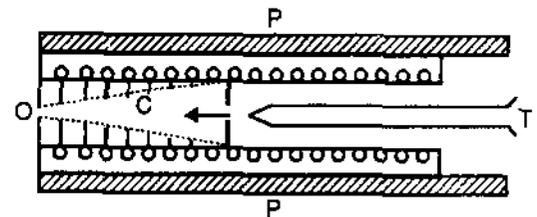


Fig. 6

• 5.3. EMISSIVE POWER

The radiant energy of all wavelengths emitted per unit time per unit surface area of the radiating body is known as 'emissive power'. If $e_\lambda d\lambda$ is the radiant energy between the wavelengths λ and $\lambda + d\lambda$, emitted per unit time per unit surface area of a body of temperature T .

Absorptive Power : The absorptive power of a surface for a particular wavelength, is equal to the ratio of the radiant energy absorbed by a given area in a given time to the total energy incident on the same area in same time within a unit wavelength range. It is denoted by a_λ .

Kirchhoff's Law : According to this law, the ratio of emissive power to the absorptive power for the radiations of a given wavelength at a given temperature is same for all bodies and this ratio is equal to the emissive power of a perfectly black body at the same temperature.

Proof : Let us consider a body placed in an isothermal enclosure. The radiation of wavelength lying between λ and $\lambda + d\lambda$, is incident on unit surface area per second. Let dQ be the radiant energy and a_λ and e_λ are the absorptive and emissive power, respectively.

The radiant energy absorbed by unit surface area of the body per second $= a_\lambda dQ$.

The reflected part of incident energy $= (1 - a_\lambda) dQ$.

Amount of energy emitted per second by per unit surface area due to its temperature = $e_\lambda d\lambda$.

Therefore, the total energy emitted by unit area per second

$$= (1 - a_\lambda) dQ + e_\lambda d\lambda$$

This must be equal to the incident energy per unit area per second. Thus,

$$(1 - a_\lambda) dQ + e_\lambda d\lambda = dQ \quad \dots(1)$$

For perfectly black body $a_\lambda = 1$.

If E_λ is the emissive power of this body then

$$E_\lambda d\lambda = dQ \quad \dots (2)$$

From equation (1),

$$e_\lambda d\lambda = a_\lambda dQ \quad \dots(3)$$

From equations (2) and (3), we get

$$e_\lambda d\lambda = a_\lambda E_\lambda d\lambda$$

or

$$\frac{e_\lambda}{a_\lambda} = E_\lambda = \text{constant}$$

This is Kirchhoff's law. From this expression, it is clear that if emission power e_λ of a body is greater, then absorptive power a_λ will be greater. **This means that good absorbers of radiation are also good emitters of radiation.**

Importance : Some practical illustrations of Kirchhoff's law are given below :

(i) If a polished metal ball with a spot of platinum black on it, is heated to about 1000°C and then taken to a dark room, it is found that the black spot shines much more than the polished surface.

(ii) A green glass appears green because it reflects green light while absorbs red colour. But when a green glass is heated then it glows with red light.

(iii) The best application of Kirchhoff's law was made in the explanation of Fraunhofer lines. A large number of dark lines are obtained in the spectrum of sun. These lines are known as Fraunhofer lines. The light from the central part of the sun has a continuous spectrum without dark lines. When this light passes through the cooler atmosphere in which the elements like H_2 , N_2 , O_2 etc. are present in the gaseous state, then these elements absorb radiations of those wavelengths which they themselves emit when heated to a high temperature. As a result, those wavelengths which absorbed by the atmosphere elements are missed from the sun spectrum and dark lines are obtained in their places.

• STUDENT ACTIVITY

1. Explain emissive power.

2. Define absorptive power.

3. What is black body ?

4. Define black body radiation.

5. Explain Fery's black body.

6. Explain Wien's black body.

• 5.4. STEFAN'S LAW

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

$$E = \sigma T^4$$

where σ is constant and this constant is known as Stefan's constant. Boltzmann explained this law theoretically from thermodynamic consideration. Therefore, it is also called 'Stefan-Boltzmann law'.

Let a black body A at temperature T is surrounded by another black body B at absolute temperature T_0 .

In this position, the amount of heat lost by black body $A = \sigma T^4$
and amount of heat absorbed by black body A from black body

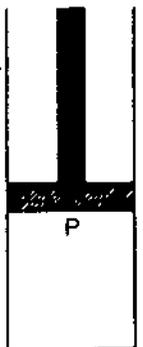
$$B = \sigma T_0^4$$

Net amount of heat lost by A per second per square centimetre

$$= \sigma(T^4 - T_0^4)$$

Now we have to prove this relation thermo- dynamically.

Thermodynamical Proof : Let us consider a cylindrical enclosure of uniform cross-section with perfectly reflecting walls and perfectly reflecting



B
Fig. 6

moving piston. Let this enclosure is filled with black body radiation of density u at uniform temperature T . If V be the volume of cylinder and P be the pressure of radiation exerted on the walls which is equal to one third of the energy density *i.e.*,

$$P = \frac{1}{3} u$$

The total energy of radiation = energy per unit volume \times volume

$$U = u \times V \quad \dots(2)$$

Let a small amount of heat dQ flows in the cylinder from outside, due to this the piston moves out and at this time the volume is changed by an amount dV . If dU is the change in the internal energy of radiation and dW is the work done, then according to first law of thermodynamics.

$$\begin{aligned} dQ &= dU + dW \\ &= dU + PdV \end{aligned} \quad \dots(3)$$

But $U = uV$ and $dW = PdV$

Therefore,

$$\begin{aligned} dQ &= d(uV) + PdV \\ dQ &= d(uV) + \frac{1}{3} udV \quad \left[\because P = \frac{1}{3} u \right] \\ &= udV + Vdu + \frac{1}{3} udV \\ &= Vdu + \frac{4}{3} udV \end{aligned} \quad \dots(4)$$

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

$$\begin{aligned} dS &= \frac{dQ}{T} \\ \therefore dS &= \frac{1}{T} \left[Vdu + \frac{4}{3} udV \right] \\ \text{or } dS &= \frac{V}{T} du + \frac{4u}{3T} dV \end{aligned} \quad \dots(5)$$

From this relation it is clear that S is a function of two independent variables u and V *i.e.*,

$$\begin{aligned} S &= f(u, V) \\ dS &= \frac{\partial S}{\partial u} du + \frac{\partial S}{\partial V} dV \end{aligned} \quad \dots(6)$$

Comparing equations (5) and (6), we get

$$\frac{\partial S}{\partial u} = \frac{V}{T} \quad \text{and} \quad \frac{\partial S}{\partial V} = \frac{4u}{3T} \quad \dots(7)$$

Since dS is a perfect differential, so we have,

$$\begin{aligned} \frac{\partial^2 S}{\partial u \partial V} &= \frac{\partial^2 S}{\partial V \partial u} \\ \therefore \frac{\partial}{\partial u} \left(\frac{\partial S}{\partial V} \right) &= \frac{\partial}{\partial V} \left(\frac{\partial S}{\partial u} \right) \end{aligned} \quad \dots(8)$$

From equations (7) and (8), we get

$$\frac{\partial}{\partial u} \left(\frac{4u}{3T} \right) = \frac{\partial}{\partial V} \left(\frac{V}{T} \right) \quad \dots(9)$$

As T is independent of V and depends on u , so by (9)

$$\begin{aligned} \frac{4}{3} \frac{1}{T} - \frac{4}{3} \frac{u}{T^2} \frac{\partial T}{\partial u} &= \frac{1}{T} \\ \frac{1}{3} \cdot \frac{1}{T} - \frac{4}{3} \frac{u}{T^2} \frac{\partial T}{\partial u} & \\ \frac{\partial u}{u} &= 4 \cdot \frac{\partial T}{T} \end{aligned}$$

On integrating, we get

$$\log u = 4 \log T + \log A$$

where $\log A$ is the constant of integration.

$$\therefore u = AT^4 \quad \dots(10)$$

Now it can be shown that the total rate of emission of radiant energy per unit area is related with the energy density by the relation.

$$E = \frac{1}{4} uc$$

$$\therefore E = \frac{1}{4} AcT^4$$

$$\text{or } E = \sigma T^4$$

where $\sigma = \frac{1}{4} Ac$ is constant and this constant is known as Stefan's constant.

Experimental Verification of Stefan's Law : Stefan's law has been experimentally verified by Lummer and Pringsheim. Their experimental arrangement is shown in the figure (7). They investigated the emission from a black body over a range of temperature varying from 100°C to 1300°C.

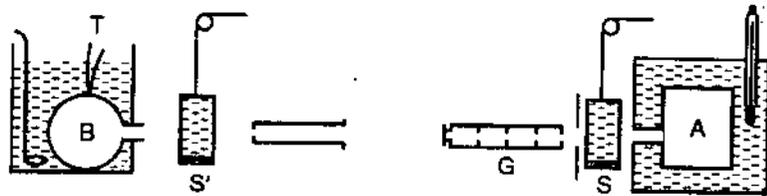


Fig. 7

It consists of two sources A and B of black body radiation. The body A is double-walled copper vessel blackened inside and having boiling water in the space between the walls and the body B is a spherical copper shell blackened inside and heated in a nitre bath between temperatures 100°C and 600°C. A thermometer T is used to measure its temperature. S and S' are water cooled shutters. G is the bolometer which is used to measure the radiant energy and can be moved on a scale.

First of all, the shutter S is removed. Due to this the galvanometer received the radiation from the black body A and the deflection in the galvanometer of the bolometer is noted. Take the different readings by putting G at different distances from A. We see that the deflection varies inversely as the square of the distance and the deflection is proportional to the energy of radiation falling on the bolometer.

Now the nitre bath is heated to a steady temperature T and the shutter S' is removed. Due to this the radiation from B falls on the bolometer. In this position, let d is the deflection in the galvanometer and T_0 be the temperature of the shutter S'. Here we find that the radiant energy received by the bolometer from the body B is same as would have been if the temperature of the shutter S' itself were raised from T_0 to T .

According to Stefan's law, the deflection in the galvanometer is directly proportional to $(T^4 - T_0^4)$.

$$\text{Thus, } d \propto (T^4 - T_0^4)$$

Here the temperature of the shutter S' is kept at 290 K. Therefore,

$$d \propto (T^4 - 290^4)$$

$$\text{or } d = \sigma (T^4 - 290^4)$$

This is the Stefan's law. Hence the Stefan's law is verified.

• 5.5. STEFAN-BOLTZMANN LAW

If T and T_0 are the absolute temperatures of the black body and its surrounding medium respectively, then the radiant energy lost per second per unit area by a black body is given by

$$E = \sigma (T^4 - T_0^4)$$

This is Stefan-Boltzmann law. Let T be greater than T_0 by a small amount x , i.e.,

$$T - T_0 = x$$

$$\text{or } T = T_0 + x$$

Therefore,

$$E = \sigma [(T_0 + x)^4 - T_0^4]$$

$$= \sigma [4T_0^3 x + 6T_0^2 x^2 + 4T_0 x^3 + x^4]$$

Since x is small, therefore the terms $6T_0^2 x^2$, $4T_0 x^3$ and x^4 can be neglected. Therefore,

$$E = 4\sigma T_0^3 x$$

or $E = 4\sigma T_0^3 (T - T_0)$

or $E \propto (T - T_0)$

From this expression, it is clear that the rate of loss of heat is very small. This is Newton's law of cooling.

The Determination of Stefan's Constant

σ : The experimental arrangement is shown in the figure (8). It consists of a hollow metallic hemisphere H blackened inside and placed in a wooden box W , lined with tin, which is used as a steam chamber. T_1 and T_2 are the thermometers used to measure the temperature of the chamber. The hemisphere H rests symmetrically on a platform AB which has a small hole at the centre. A disc D made by silver blackened at its top surface can be fitted or taken out from the hole. One junction of a silver-constantan thermocouple is soldered to the lower surface of D , while the other is placed in a water bath C . G is the galvanometer which is connected in the thermocouple circuit with resistance R in series.

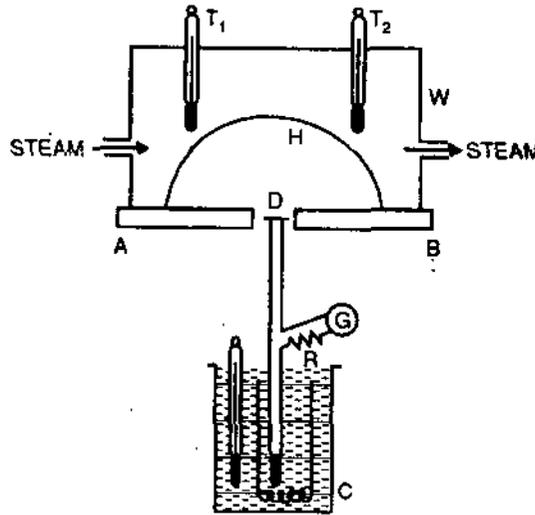


Fig. 8

Theory : When the inner surface of H is heated by passing steam, then it acts as a black body radiator. Due to this, the disc D absorbs radiation emitted by H and hence its temperature increases continuously and a temperature difference is produced in the two junctions of thermocouple. In this position, the galvanometer shows a deflection.

If T_1 be the steady state temperature of H and T_0 of disc D , when it is just exposed to radiation from H .

Therefore, from Stefan-Boltzmann law the net energy gained by the disc D per second

$$= EA \quad [A \text{ is the area of disc}]$$

$$= \sigma (T_1^4 - T_0^4) A \text{ Joule}$$

$$= \frac{\sigma (T_1^4 - T_0^4) A}{J} \text{ kilo cal.}$$

If m be the mass of disc, C is the specific heat and $\frac{dT}{dt}$ the rate of change of temperature then

net energy gained per second will be $mc \frac{dT}{dt}$. Hence,

$$mc \frac{dT}{dt} = \frac{\sigma A (T_1^4 - T_0^4)}{J} \quad \dots(1)$$

or $\sigma = \frac{Jmc}{A (T_1^4 - T_0^4)} \frac{dT}{dt} \text{ watt m}^{-2} \text{ k}^{-4}$

Now we have to calculate the value of $\frac{dT}{dt}$.

The experiment consists of two steps :

(i) **Calibration of Thermo-couple :** First of all, the silver disc is kept in position in the hole, Now the water bath C is heated to a suitable temperature. Due to temperature difference of junctions of thermo couple, the galvanometer shows deflection. Let x is the deflection of galvanometer at temperature T . A graph is plotted

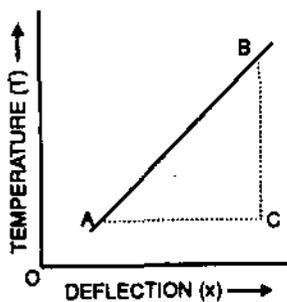


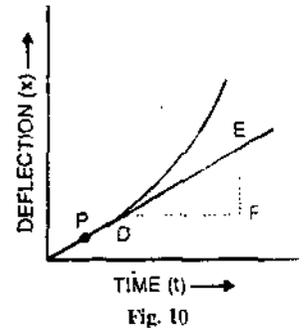
Fig. 9

between temperature T and deflection x , then a straight line is obtained whose slope is $\frac{dT}{dx}$.

$$\text{Thus, } \frac{dT}{dx} = \frac{BC}{AC} \quad \dots (2)$$

During this part, disc acts as the cold junction of the thermo-couple.

(ii) Measurement of $\frac{dT}{dt}$: For this, the disc D is removed from the hole and steam is passed through the box W . When the temperature becomes steady then the disc is again placed. In this position, the disc absorbs radiation from H and its temperature increases and hence a deflection in the galvanometer is obtained: A graph is plotted between deflection (x) and time (t). Now a tangent is drawn to the curve at point P near the origin.



The slope of the curve is

$$\frac{dx}{dt} = \frac{EF}{DF} \quad \dots (3)$$

From equations (2) and (3), we get

$$\frac{dT}{dt} = \frac{dT}{dx} \times \frac{dx}{dt} = \frac{BC}{AC} \times \frac{EF}{DF}$$

Thus, if the values of $\frac{BC}{AC}$ and $\frac{EF}{DF}$ are known, then $\frac{dT}{dt}$ can be calculated, and hence from equation (1) the value of Stefan's constant σ can be obtained.

• 5.6. SPECTRUM OF BLACK BODY RADIATION

The distribution of energy among the various wavelengths at different temperatures in black body radiation was studied by Lummer and Pringsheim in 1899, i.e., how the emissive power E_λ varies with λ and T .

It was found that when a body is heated, its colour changes with change in temperature. For example, a blackened platinum wire appears red at a particular temperature. When the temperature is increased it becomes orange and then yellow and then white. This shows clearly that the radiation of maximum intensity shifts towards shorter wavelength side when the temperature of the body increases. The experimental arrangement is shown in the figure (11).

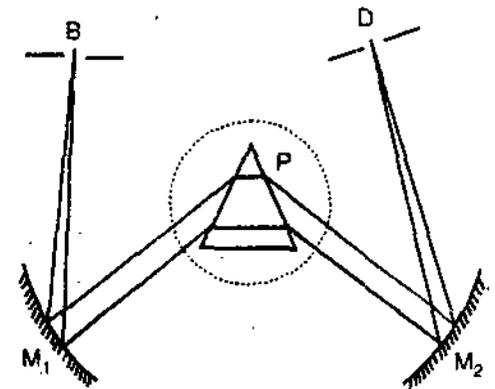


Fig. 11

The radiation from the black body B falls on a flint glass prism P by means of a concave mirror M_1 . The emerging beam falls on the concave mirror M_2 which directs it on to a Lummer-Kurlbaum bolometer D . The bolometer was connected to a galvanometer and the deflections in the galvanometer corresponding to different wavelengths (λ) were noted by rotating the prism table. Then curves were plotted between E_λ and λ . The experiment was done with the black body at different temperatures. The curves obtained are shown in fig. (12). These curves show the following important features:

(i) The energy is not uniformly distributed in the radiation spectrum of a black body.

(ii) The intensity of radiation increases with increase of wavelength and becomes maximum at a particular wavelength. After this particular wavelength, the intensity of heat radiation decreases.

(iii) The point of maximum energy shifts towards the shorter wave-lengths on increasing the temperature. This is called Wien's displacement law.

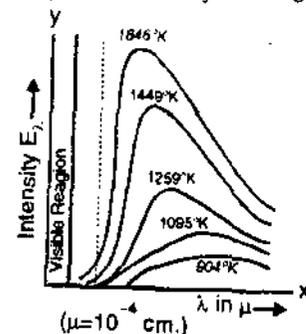


Fig. 12

(iv) The total energy of radiation at a given temperature is given by the area between curve and the horizontal axis. This area increases according to the fourth power of absolute temperature. This is called Stefan's law.

Explanation of Classical Theory

(1) **Wien's Law** : Wien in 1893, investigated the energy distribution over different wavelengths. He showed that the energy E_λ at wavelength λ in the spectrum of black body at absolute temperature T , is given by

$$E_\lambda = \frac{1}{\lambda^5} f(\lambda T)$$

where $f(\lambda T)$ is a function of the product (λT) . Now we have to calculate the value of this function f , with the help of the following assumptions.

(i) Every molecule in the radiator emits a radiation of a single wavelength only, which depends upon the velocity of molecule.

(ii) Intensity of wave is a function of the velocity of the molecule.

(iii) The intensity E_λ whose wavelength lies between λ and $(\lambda + d\lambda)$, is proportional to the number of vibrating molecules with period.

On the basis of above assumptions Wien found that

$$f(\lambda T) = Ae^{-B/\lambda T}$$

where A and B are constants. This formula is applicable for the shorter wavelength region only.

(2) **Reyleigh-Jeans formula** : From principles of statistical mechanics, they obtained the formula

$$E_\lambda d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda$$

where k is the Boltzmann's constant and E_λ is the energy density between λ and $\lambda + d\lambda$.

They considered that the black body radiator consists of electromagnetic waves of all wavelengths between 0 and ∞ which form standing waves due to reflection at the walls. This formula gives $E_\lambda \rightarrow \infty$, if $\lambda \rightarrow 0$. Thus this formula agrees with experimental result in the long wavelength range only.

(3) **Planck's Law** : In 1900, Planck gave the revolutionary idea that the radiation is not emitted continuously but discontinuously in the form of energy packets, called 'quanta' of energy $h\nu$, where ν is the frequency of radiation and h is Planck's constant. Thus the emitted energy will be $h\nu$, $2h\nu$, $3h\nu$, ... on the basis of quantum theory, he gave the formula

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5 (e^{hc/\lambda kT} - 1)}$$

where c is the velocity of light and k is the Boltzmann's constant and E_λ is energy density between λ and $\lambda + d\lambda$.

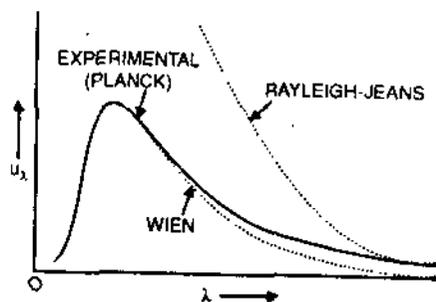


Fig. 13

5.7. PLANCK'S MECHANISM OF EMISSION AND ABSORPTION OF RADIATION

Wein's displacement law and Rayleigh-Jeans's formula could not explain the entire shape of the curves giving the energy distribution in black body radiation. Planck in 1900, said that a black body chamber is filled up not only with radiation but also with the molecules of a perfect gas.

He assumed that the exchange of energy can not take place between radiation and gas molecules directly and atoms of the black body behave as oscillators, each with a characteristic frequency of oscillation. The oscillators take energy from radiation and transfer some part of it to the molecules when they collide with them. These oscillators are responsible for the emission of radiation.

Quantum mechanically, the exchange of energy by oscillators do not take place continuously but takes place discontinuously or we can say that the oscillators will emit energy only when the energy absorbed is a certain minimum quantity.

Planck made the following two assumptions :

(i) The oscillator can have only discrete energies given by

$$E = nh\nu$$

where ν is the frequency of oscillator, h is Planck's constant and n is an integer called quantum number. Thus, the oscillator can have only quantised energies $h\nu$, $2h\nu$, $3h\nu$, ... $nh\nu$.

(ii) The oscillators do not emit or absorb energy continuously but only in jumps. Thus

$$\Delta E = (\Delta n) h\nu \quad \Delta n = 1, 2, 3, \dots$$

Average Energy of Planck's Oscillator : The relative probability that an oscillator has the energy $h\nu$ at temperature T is given by Boltzmann factor $e^{-h\nu/KT}$. Let $N_0, N_1, N_2 \dots N_r$ are the number of oscillators having energies $0, h\nu, 2h\nu \dots rh\nu$, respectively. Then we have

$$N_r = N_0 e^{-rh\nu/KT}$$

The total number of oscillators is given by

$$\begin{aligned} N &= N_0 + N_1 + N_2 + \dots \\ &= N_0 (1 + e^{-h\nu/KT} + e^{-2h\nu/KT} + \dots) \\ &= \frac{N_0}{1 - e^{-h\nu/KT}} \end{aligned} \quad \dots(1)$$

The total energy of oscillator is

$$\begin{aligned} \epsilon &= (N_0 \times 0) + (N_1 \times h\nu) + (N_2 \times 2h\nu) + \dots \\ &= (N_0 \times 0) + (N_0 e^{-h\nu/KT} \times h\nu) + (N_0 e^{-2h\nu/KT} \times 2h\nu) \\ &= (N_0 e^{-h\nu/KT} h\nu (1 + 2e^{-2h\nu/KT}) + 3e^{-2h\nu/KT} + \dots) \\ &= N_0 e^{-h\nu/KT} \frac{h\nu}{(1 - e^{-h\nu/KT})^2} \end{aligned} \quad \dots(2)$$

The average energy of an oscillator is given by

$$\begin{aligned} \bar{\epsilon} &= \frac{\epsilon}{N} = \frac{e^{-h\nu/KT} (h\nu)}{1 - e^{-h\nu/KT}} \\ \bar{\epsilon} &= \frac{h\nu}{e^{h\nu/KT} - 1} \end{aligned} \quad \dots(3)$$

This is the required expression for the average energy of a Planck's oscillator.

Planck's Radiation Formula : The average energy of a Planck's oscillator is given by

$$\bar{E} = \frac{h\nu}{e^{h\nu/KT} - 1}$$

The number of oscillators per unit volume in the frequency range ν and $\nu + d\nu$ is

$$= \frac{8\pi\nu^2}{c^3} d\nu \quad \dots(4)$$

The energy density of radiation in the frequency range ν to $\nu + d\nu$ is

$$\begin{aligned} E_\nu d\nu &= \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{(e^{h\nu/KT} - 1)} d\nu \\ \text{or} \quad E_\nu d\nu &= \frac{8\pi h\nu^3}{c^3} \cdot \frac{1}{(e^{h\nu/KT} - 1)} d\nu \end{aligned} \quad \dots(5)$$

This is known as Planck's radiation formula in terms of frequency. To express it in terms of wavelength, we have

$$\begin{aligned} \nu &= \frac{c}{\lambda} \\ \therefore d\nu &= -\frac{c}{\lambda^2} d\lambda \end{aligned}$$

and since an increase in frequency corresponds to a decrease in wavelength,

$$E_\nu d\nu = -E_\lambda d\lambda$$

Therefore,

$$E_\lambda d\lambda = \frac{8\pi h}{c^3} \left(\frac{c}{\lambda}\right)^3 \left(\frac{c}{\lambda^2} d\lambda\right) \frac{1}{(e^{hc/\lambda KT} - 1)}$$

or

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{hc/\lambda KT} - 1} \quad \dots(6)$$

This is Planck's radiation formula in terms of wavelength.

Explanation of Energy Distribution by Planck's Formula : Wien's Law and Rayleigh-Jeans Law are Special Cases :

(i) **Wien's Law :** When λ is very small, then $e^{hc/\lambda KT} \gg 1$ i.e., 1 can be neglected in comparison of $e^{hc/\lambda KT}$. Hence from equation (6), we get

$$E_\lambda d\lambda = \frac{8\pi\lambda c}{\lambda^5} e^{-hc/\lambda KT} d\lambda$$

Let $8\pi hc = A$ and $\frac{hc}{K} = B$, then

$$E_\lambda d\lambda = \frac{A}{\lambda^5} e^{-B/\lambda T} d\lambda \quad \dots(7)$$

This is Wien's formula which is applicable for short wavelengths.

(ii) **Rayleigh-Jeans Formula :** When λ is very large, then $e^{hc/\lambda KT} = 1 + \frac{hc}{\lambda KT}$, so that equation (6), gives

$$E_\lambda d\lambda = \frac{8\pi hc}{\lambda^5} \cdot \frac{d\lambda}{\left(1 + \frac{hc}{\lambda KT} - 1\right)} = \frac{8\pi KT}{\lambda^4} d\lambda$$

This is Rayleigh-Jeans formula which is applicable for long wavelengths.

• 5.8. SOLAR CONSTANT

The temperature of sun is very high. Due to this high temperature, it radiates energy in all directions. This energy is known as radiant energy. A part of this energy, which reaches the earth is known as solar energy. A constant quantity of this solar energy is known as **solar constant** and it may be defined as "the amount of solar energy absorbed by earth (perfectly black body) per minute by one square centimetre of surface placed normally to the sun's rays and placed at the mean distance of earth from sun in the absence of atmosphere."

Determination of Solar Constant : The device which is used to determine the solar constant is known as 'Pyrheliometer'. Angstrom's pyrheliometer is shown in the fig. (14). It consists of two thin exactly similar strips of platinum S_1 and S_2 . One of them is open to receive radiation from the sun normally, while the other is shielded by a screen H . The junction of a copper-constantan thermo-couple are attached to the backs of S_1 and S_2 .

Working : When both S_1 and S_2 are at same temperature then galvanometer shows no deflection. When radiation of sun falls on S_1 , then its temperature increases and galvanometer shows deflection. In this position, the current is passed through S_2 and is so adjusted that the deflection of the galvanometer reduces to zero. The temperatures of S_1 and S_2 are the same and it indicates that they must be receiving energy at the same rate.

Let I is the current flowing through the battery circuit and E is the potential difference across S_2 , then heat supplied to S_2 is

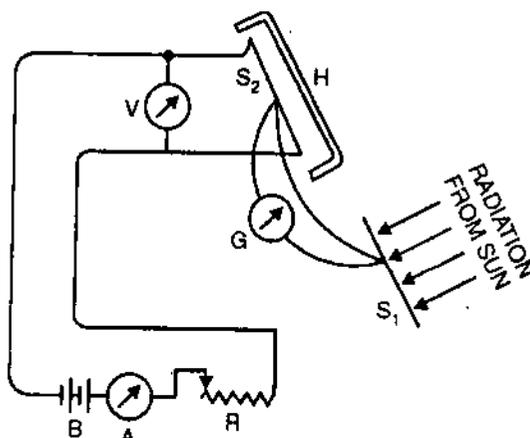


Fig. 14

$$\begin{aligned}
 &= EI \text{ joule/sec.} \\
 &= EI \times 10^7 \text{ ergs/sec.} \\
 &= \frac{EI}{J} \times 10^7 \text{ cal/sec.} \quad \dots(1) \\
 &= \frac{EI}{4.2} \text{ cal/sec.}
 \end{aligned}$$

Let b and l are the breadth and length of the strip, let a be its absorption coefficient and H is the incident radiation per second per square cm, then energy absorbed by the strip per second

$$= Halb \quad \dots(2)$$

From equations (1) and (2), we get

$$\begin{aligned}
 Halb &= \frac{EI}{J} \times 10^7 \\
 H &= \frac{EI}{albj} \times 10^7
 \end{aligned}$$

This gives the intensity of radiation in calories from which we can find the **solar constant**.

The experiment is repeated by S_1 and S_2 , i.e., by exposing S_2 and by shielding S_1 . Knowing the surface area and making corrections due to absorption by the earth's atmosphere the solar constant can be calculated as follows :

To eliminate the effect of absorption of earth's atmosphere the value of the solar constant S is found for different elevations of the sun on the same day under constant sky conditions, then

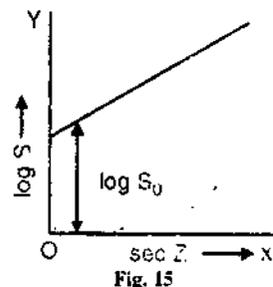
$$S = S_0 a^{\sec Z}$$

and so is the true value of solar constant where ' a ' is called transmission coefficient and Z is the zenith distance of angular altitude of sun.

Taking logarithm,

$$\log S = \log S_0 + \sec Z \log a$$

If a graph is plotted between $\log S$, and $\sec Z$, then a straight line is obtained. Its intercepts on the y-axis gives $\log S_0$. From this we can calculate S_0 .



Temperature of Sun : The central part of the sun is very hot. This part is known as 'photosphere'. It is surrounded by a comparatively cooler atmosphere and known as 'chromosphere'. Let r and T are the radius and temperature of the photosphere of the sun. If we suppose it to be a black body, Stefan's law, amount of heat radiated by it per unit time is

$$4\pi r^2 \sigma T^4$$

where σ is Stefan's constant. Let r be the mean distance of earth from the sun, the emitted radiated energy will be spread over a sphere of surface area $4\pi R^2$. Hence the energy received per unit time per unit surface area of earth

$$= \frac{4\pi r^2 \times \sigma T^4}{4\pi R^2}$$

But this is the solar constant S , therefore

$$S = \frac{4\pi r^2 \times \sigma T^4}{4\pi R^2}$$

$$T^4 = \frac{S}{\sigma} \left(\frac{R}{r} \right)^2$$

If the values of S , R , r and σ are known, then the temperature of the sun can be calculate.

• STUDENT ACTIVITY

7. Define solar constant.

8. How will you get the temperature of Sun ?

9. Using Wien's displacement law, estimate the temperature of the Sun. Given, $\lambda_m = 4900 \text{ \AA}$ and Wien's constant = 0.292 cm. k .

Ans. 5959 K.

• 5.9. DULONG AND PETIT LAW

In 1819, Dulong and Petit studied the specific heat of various substances in solid state and gave a law. This law is known as Dulong and Petit's law. According to this law "the product of atomic weight and the specific heat (*i.e.*, atomic heat) of an element at constant volume remains constant for a number of elements in solid state and is equal to 5.96 (= 6) cal/gram-atom-K".

Deduction of Dulong and Petit's law from Classical (Kinetic) Theory : According to classical kinetic theory, the atoms of a solid substance, are at rest under the action of their mutual attraction and repulsions at the absolute zero temperature.

The energy of solids in this state is assumed to be zero. When the temperature is raised then the atoms are set into vibrations about their mean positions and the restoring force proportional to

the displacement is produced as the amplitude of vibration is not too large. This means that the vibrations of the atoms are simple harmonic in nature.

In this position, the energy is

$$\frac{1}{2} m\dot{x}^2 + \frac{1}{2} Kx^2$$

where K is the force constant and x is the displacement. Here the first term represents the kinetic energy and the second term represents the potential energy. But in case of S.H.M., the average kinetic energy is equal to the average potential energy. This means that the average energy corresponding to one vibration is equal to twice the kinetic energy corresponding to one degree of freedom. Thus we can say that the vibration of an atom in a elastic solid along one co-ordinate is equivalent to two degrees of freedom.

According to law of equipartition of energy, the average energy associated with the motion of an atom along one co-ordinate

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

where k is the Boltzmann constant.

If each atom is free to vibrate along three co-ordinate axes, then the total average energy of each atom

$$= 3kT$$

The total energy of one gram atom of solid containing N atoms is

$$\begin{aligned} E &= 3NkT \\ &= 3RT \end{aligned} \quad \dots(1)$$

where $R = Nk =$ gas constant for one gram atom.

If the whole energy given to the atom is used in increasing the energy of vibration of atom and during the rise in temperature the volume of the substance remains constant, then the atomic heat at constant volume is given by

$$C_v = \frac{dE}{dT} = 3R \quad \dots(2)$$

This means that the specific is constant and independent of temperature.

We have

$$\begin{aligned} R &= 1.9856 \text{ cal per gm atom} \\ C_v = 3R &= 3 \times 1.9856 \\ &= 5.9468 \end{aligned}$$

This is Dulong and Petit's law.

Variation of Specific Heat with Temperature

Applicability of the Law : According to Dulong's and Petit's law, the specific heat of all solids must be about 6 cal/(g-atom-K) and it should not vary with temperature. Since atomic weight of an element is constant, its specific heat must be constant *i.e.*, the value of specific heat of various elements should be same at all temperatures. But in fact, it is not true. It has been found by experiments that the specific heat of all substances varies with temperature.

It is found that specific heat of a substance decreases with decrease in temperature and tends to be zero at absolute temperature. If we plot a graph between specific heat and temperature for diamond, aluminium and silver then the curves obtained are shown in the fig. (16). Carbon whose specific heat at ordinary temperature is 1.76, show an increase in its value towards 6 as the temperature is raised and finally the specific heat of carbon becomes 6 at high temperature but it is less than 6 at low temperature.

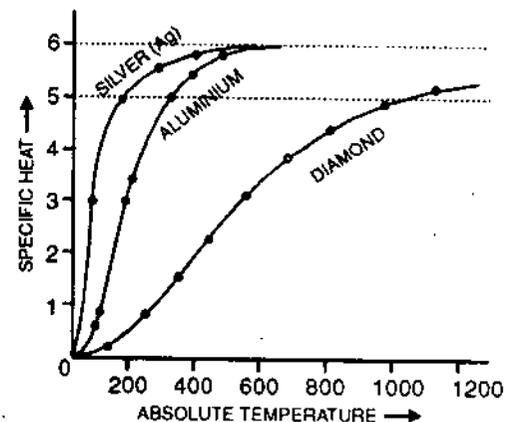


Fig. 16

The experimental observation of specific heat at low temperature shows that the specific heat decreases slowly with decrease of temperature and below a certain temperature the specific heat decreases and becomes zero at absolute temperature.

From above it is clear that Dulong and Petit's law is true at high temperature and completely fails at very low temperatures.

• 5.10. EINSTEIN'S QUANTUM THEORY OF SPECIFIC HEAT

The explanation of variation of specific heat of solids with temperature was made by Einstein in 1907 on the basis of quantum theory. According to this theory, heat is radiated in the form of discrete particles, known as photons. Each photon has energy equal to $h\nu$ where h is the Planck's constant and ν is the frequency of heat radiations.

Einstein considered that a solid is constituted of atoms. These atoms are at rest under the action of the mutual attraction and repulsion at absolute zero temperature. In this position, the energy of solid is zero. When the solid is heated, the atoms vibrate about their mean positions. The frequency of these vibrations is same. He also considered that a solid has 3 degrees of freedom like a molecule of a mono-atomic gas. On this basis, the average energy of an oscillator per degree of freedom is

$$\frac{h\nu}{e^{h\nu/KT} - 1}$$

i.e., the energy per degree of freedom is not KT . The total energy of a gram-atom of the solid consisting of N atoms is

$$E = \frac{3N h\nu}{e^{h\nu/KT} - 1}$$

Therefore, the specific heat is given by

$$\begin{aligned} C_v &= \frac{dE}{dT} = 3N h\nu \frac{e^{h\nu/KT} \left(\frac{h\nu}{KT^2} \right)}{(e^{h\nu/KT} - 1)^2} \\ &= 3NK \left(\frac{h\nu}{KT} \right)^2 \frac{e^{h\nu/KT}}{(e^{h\nu/KT} - 1)^2} \end{aligned}$$

But $NK = R$

$$C_v = 3R \left(\frac{h\nu}{KT} \right)^2 \frac{e^{h\nu/KT}}{(e^{h\nu/KT} - 1)^2}$$

Let $\frac{h\nu}{K} = \theta_E$ where θ_E is known as Einstein's temperature, then

$$C_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad \dots(1)$$

This is the required expression for Einstein's specific heat. The characteristics of experimentally observed variation of specific heat of solids are as follows :

(1) **At high temperature** ($T \gg \theta_E$) : We have, $\frac{\theta_E}{T} \ll 1$, so that

$$e^{\theta_E/T} = 1 + \frac{\theta_E}{T}, \text{ then equation (1) gives}$$

$$C_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{1 + \frac{\theta_E}{T}}{\left(\frac{\theta_E}{T} \right)^2} \approx 3R \quad \dots(2)$$

This is agreement with Dulong and Petit law which agrees with experiment at high temperature.

(2) **At low temperature** ($T \ll \theta_E$) : In this case, we have $\frac{\theta_E}{T} \gg 1$, so that $e^{\theta_E/T} \gg 1$. Then equation (1), gives

$$C_v \approx 3R \left(\frac{\theta_E}{T} \right)^2 e^{-\theta_E/T} \quad \dots(3)$$

From this it is clear that when $T \rightarrow 0$ the specific heat C_V also tends to zero, which is agreement with the experimental results.

Limitations : The Einstein's theory fails at very low temperature. At very low temperature the specific heat is proportional to T^3 . This agreement is due to the neglect of the mutual forces exerted by the atoms to each other. This difficulty was removed by Debye in 1912 and give a specific heat formula which is agreement with experiment over the whole temperature range.

• 5.11. DEBYE'S THEORY OF SPECIFIC HEAT OF SOLIDS

Debye considered the solid as an elastic body capable of vibrating in various possible modes. According to him the atoms do not vibrate independently with same frequency. The oscillations belong to the entire solid and frequencies modes of oscillations vary from zero to certain maximum value ν_m which is a characteristic of the solid. According to Debye's theory, the number of modes of vibration are counted by a method similar to that applied to electromagnetic waves in a cavity.

When a continuous solid is subjected to elastic vibrations, two kinds of vibrations are produced:

(i) Transverse vibrations, (ii) Longitudinal vibrations.

The number of modes of longitudinal vibrations per unit volume with frequencies between ν and $\nu + d\nu$

$$= \frac{4\pi\nu^2 d\nu}{c_l^3}$$

where c_l is the velocity of longitudinal vibrations.

The number of modes of transverse vibrations per unit volume with frequencies between ν and $\nu + d\nu$

$$= \frac{8\pi\nu^2 d\nu}{c_t^3}$$

where c_t is the velocity of transverse vibrations.

Since transverse vibrations have two independent directions of vibrations *i.e.*, they are equivalent to two waves polarised at right angles to each other.

Therefore, the number of independent vibrations per unit volume with frequencies between ν and $\nu + d\nu$

$$= 4\pi \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu$$

If V is the volume of one gram molecule of the solid, the number of modes of vibrations with frequencies between ν and $\nu + d\nu$

$$= 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu$$

The total number of independent modes of vibrations is given by

$$\int_0^{\nu_m} 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu \quad \dots (1)$$

The upper limit of integration is not infinity because Debye considered that the frequencies can only reach a definite upper limit ν_m . This limit is chosen so that the total number of possible independent vibrations is equal to the number of vibrations of the separate atom in the solid. If there are N atoms in volume V then the possible number of vibrations will be equal to $3N$, because each atom have three degrees of freedom. Thus

$$\begin{aligned} \int_0^{\nu_m} 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu &= 3N \\ 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \frac{\nu_m^3}{3} &= 3N \\ 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] &= \frac{9N}{\nu_m^3} \quad \dots (2) \end{aligned}$$

Now we have to calculate the energy of solid. According to quantum theory, the average energy associated with each degree of freedom

$$= \frac{h\nu}{e^{h\nu/KT} - 1}$$

The thermal energy of one gram atom of solid for frequencies between ν and $\nu + d\nu$

$$\begin{aligned} &= \frac{h\nu}{e^{h\nu/KT} - 1} \cdot 4\pi V \left[\frac{1}{c_l^3} + \frac{2}{c_t^3} \right] \nu^2 d\nu \\ &= \frac{h\nu}{e^{h\nu/KT} - 1} \cdot \frac{9N}{v_m^3} \nu^2 d\nu \quad \text{[From eq. (2)]} \\ &= \frac{9N}{v_m^3} \cdot \frac{h\nu^3 d\nu}{e^{h\nu/KT} - 1} \quad \dots(3) \end{aligned}$$

∴ The total thermal energy for one gram atom of solid is

$$\begin{aligned} E &= \int_0^{\nu_m} \frac{9N}{v_m^3} \frac{h\nu^3 d\nu}{e^{h\nu/KT} - 1} \\ &= \frac{9N}{v_m^3} \int_0^{\nu_m} \frac{h\nu^3 d\nu}{e^{h\nu/KT} - 1} \quad \dots(4) \end{aligned}$$

Let $\frac{h\nu}{KT} = x$, then $\nu = \frac{KT}{h} x$

$$d\nu = \frac{KT}{h} dx, \text{ then}$$

$$E = \frac{9N}{v_m^3} \left(\frac{KT}{h} \right)^3 KT \int_0^{x_m} \frac{x^3 dx}{e^x - 1}$$

where

$$x_m = h\nu_m / KT$$

$$E = 9NK \left(\frac{K}{h\nu_m} \right)^3 T^4 \int_0^{x_m} \frac{x^3 dx}{e^x - 1} \quad \dots(5)$$

Now, we define the Debye temperature as,

$$\theta_D = \frac{h\nu_m}{K}, \text{ so that } x_m = \frac{h\nu_m}{KT} = \frac{\theta_D}{T}$$

From equation (5), we get

$$E = 9R \frac{T^4}{\theta_D^3} \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} \quad [\because R = NK]$$

Therefore, the atomic specific heat of the solid is $C_V = \frac{dE}{dT}$

$$C_V = 9R \left[4 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3 dx}{e^x - 1} - \left(\frac{\theta_D}{T} \right) \frac{1}{e^{\theta_D/T} - 1} \right] \quad \dots(6)$$

This is the required expression for Debye's specific heat.

(i) **At high temperature** : In this case, both $x = \left(\frac{h\nu}{KT} \right)$ and $\frac{\theta_D}{T}$ are very small so that $e^x = 1 + x$ and hence $e^{\theta_D/T} = 1 + \frac{\theta_D}{T}$. Then equation (6) gives,

$$C_V = 9R \left[4 \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^2 dx - \left(\frac{\theta_D}{T} \right) \frac{1}{\theta_D/T} \right]$$

$$\begin{aligned} C_V &\approx 9R \left[4 \left(\frac{T}{\theta_D} \right)^3 \frac{(\theta_D/T)^3}{3} - 1 \right] \\ &\approx 3R \end{aligned}$$

which is Dulong-Petit law.

(ii) **At very low temperature** : In this position $\frac{\theta_D}{T} \rightarrow \infty$, then the second term in equation (6), can be neglected and upper limit can be replaced by ∞ , i.e.,

$$C_V \approx 9R \left[4 \left(\frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^3 dx}{e^x - 1} \right]$$

Here,
$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

$$\begin{aligned} \therefore C_V &\approx 9R \left[4 \left(\frac{T}{\theta_D} \right)^3 \frac{\pi^4}{15} \right] \\ &= \frac{12}{5} \frac{\pi^4 R}{\theta_D^3} T^3 \end{aligned}$$

Since θ_D is constant for solids, therefore $C_V \propto T^3$.

Thus, at very low temperature, the specific heat of solid is proportional to the cube of absolute temperature. This is known as Debye's T^3 law.

• SUMMARY

- The pressure of radiation for normal incidence is equal to the energy density.
- Black body has the property of allowing all incident rays to enter itself without reflection and not allowing them to leave again.
- Good absorbers of radiation are also good emitters of radiation.
- Oscillators will emit energy only when the energy absorbed is a certain minimum quantity.
- A constant quantity of this solar energy is known as solar constant.

• TEST YOURSELF

1. Give Bartoli's proof to show that radiation exerts pressure.
2. What is a perfectly black body? Show how it can be realised experimentally?
3. Prove Kirchhoff's law of radiation and give its importance.
4. Discuss Stefan's law of radiation and prove it from the principle of thermodynamics.
5. Verify Stefan's law of radiation experimentally.
6. Give Stefan-Boltzmann law of radiation. Prove that for small differences of temperature, Newton's law of cooling is just an approximation of the above law.
7. How is Stefan's constant determined in the laboratory?
8. Give an account of the Lummer-Pringsheim experiment on the distribution of energy in black body radiation.
9. Discuss Planck's mechanism of emission and absorption of radiation. Obtain an expression for the average energy of a Planck's oscillator. Show that Rayleigh-Jean's law and Wien's law are special cases of Planck's law.
10. Define solar constant. Explain with necessary theory how the solar constant is determined.
11. State Dulong and Petit law for the specific heat of solids and obtain it classically.
12. Explain Einstein's quantum theory of specific heat.
13. Explain Debye's theory of specific heat of solids as an improvement over the Einstein's theory.
14. For giving energy distribution in thermal spectrum, Rayleigh and Jeans considered :

(a) Quantum mechanics	(b) Statistical mechanics
(c) Dynamical mechanics	(d) All of these
15. Wien's law is a special case of Planck's law for :

(a) Smaller wavelengths	(b) Longer wavelengths
(c) All wavelengths	(d) None of these
16. Rayleigh-Jeans law is a special case of Planck's law for :

(a) Smaller wave lengths	(b) Longer wave lengths
(c) All wavelengths	(d) None of these
17. A polished metallic ball with a black spot on it is heated to a high temperature and taken into dark, then :

(a) The spot will appear brighter than the ball
(b) The spot will appear darker than the ball
(c) Both will appear equally bright
(d) None of the above
18. According to Probst theory of exchange to explain the phenomenon of radiation, the rate of radiation from a body depends on :

