

HEAT AND THERMODYNAMICS

HEAT :- (1) "Heat is the energy transferred between a system and its surroundings because of the difference in their temperatures."

(2) "Heat is a form of energy associated with molecular motion."

It is denoted by 'Q' and has units of Calorie, Joule, BTU. $1 \text{ cal} = 4.2 \text{ J}$, $1 \text{ BTU} = 252 \text{ cal}$.

THERMODYNAMICS :- "It is the branch of physics which deals with the transformation of heat energy into other forms of energy like mechanical energy, light etc."

KINETIC THEORY OF GASES :-

The behaviour of gases is well explained by the kinetic theory based on microscopic approach. The important postulates of this theory are:

- (1) A finite volume of a gas consists of very large number of molecules.
- (2) The size of the molecules is much smaller than the separation between them.
- (3) The gas molecules are in random motion and may change their direction of motion.

after every collision.

- (4) The collisions between gas molecules themselves and with the walls of container are assumed to be perfectly elastic.
- (5) The molecules do not exert force on each other except during a collision.
- (6) The pressure exerted by the gas molecules is due to their elastic collisions with the walls of the container.

PRESSURE OF A GAS :-

According to the Kinetic theory, the pressure exerted by a gas is merely the momentum transferred to the walls of the container per second per unit area due to the continuous collisions of molecules of the gas. An expression for the pressure exerted by a gas can, therefore, be obtained as follows:-

Let 'N' number of molecules each of mass 'm' of a gas are contained in a cubical vessel of side 'l' as shown in fig.-1. Any

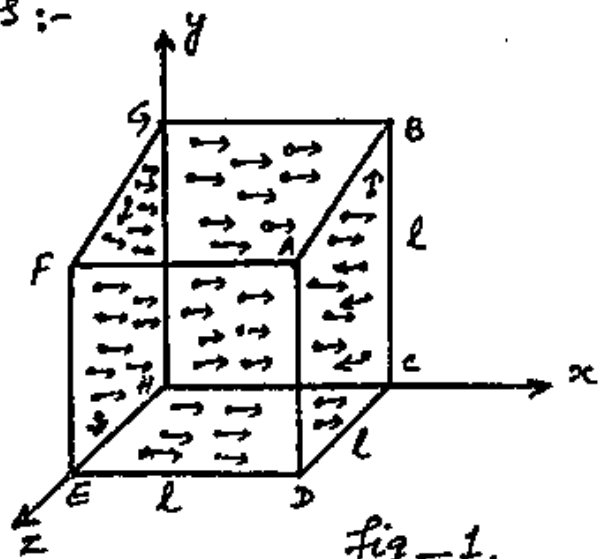


Fig.-1.

one of these molecules having velocity ' v_1 ' in a

Certain direction can be resolved into three rectangular components v_{ix} , v_{iy} , v_{iz} parallel to three co-ordinate axes x , y , and z .

Initial momentum of the molecule striking the face **ABCD** is then ' mv_{ix} '. If the collision is assumed perfectly elastic, the molecule will rebound from the face **ABCD** with the same speed. Thus each collision produces a change in momentum, which is equal to:

$$\begin{aligned} \text{Change in momentum} &= \text{Final mom.} - \text{Initial mom.} \\ &= (-mv_{ix}) - (mv_{ix}) \end{aligned}$$

$$\therefore \text{change in momentum} = -2mv_{ix} \longrightarrow (1)$$

After recoil the molecule travels to opposite face **EFGH** and collides with it, rebounds and travels back to the face **ABCD** after covering a distance $= 2l$. The time ' Δt ' between two successive collisions with face **ABCD** is:

$$\Delta t = \frac{2l}{v_{ix}} \longrightarrow (2) \quad \begin{aligned} \because S &= vt \\ (2l &= v_{ix} \Delta t) \end{aligned}$$

The eq. (2) can be used to calculate "the number of collisions per second", (or collision frequency $= f$), that the molecule will make with face **ABCD** is given by:

$$\because f = \frac{1}{\Delta t}, \quad \therefore f = \frac{v_{ix}}{2l} \longrightarrow (3)$$

Thus the "rate of change of momentum" of the molecule due to collisions with face

ABCD is given by:

Rate of change of mom. = Change in mom. in one Collision x no. of Coll. pers

or Rate of change of mom. = -x m v_{1x} x \frac{v_{1x}}{xl} = -\frac{m v_{1x}^2}{l}

According to Newton's 2nd law in terms of mom.

"the rate of change of momentum of the molecule is equal to the force applied by the wall." According to Newton's third law of motion, the force 'F_{1x}' exerted by the molecule on the face ABCD is equal and opposite to the force applied by the wall i.e.

F_{1x} = -(-\frac{m v_{1x}^2}{l}) = \frac{m v_{1x}^2}{l}

or F_{1x} = \frac{m v_{1x}^2}{l} \longrightarrow (4)

Similarly the forces due to all other molecules can be determined. Thus the total x-directed force 'F_x' due to 'N' no. of molecules of the gas moving with velocities v_1, v_2, v_3, ... v_N is:

F_x = F_{1x} + F_{2x} + F_{3x} + ... + F_{Nx}

or F_x = \frac{m v_{1x}^2}{l} + \frac{m v_{2x}^2}{l} + \frac{m v_{3x}^2}{l} + ... + \frac{m v_{Nx}^2}{l}

\therefore Pressure = \frac{Force}{Area}

\therefore P_x = \frac{F_x}{A} = \frac{F_x}{l^2} (\because A = l^2)

or P_x = \frac{1}{l^2} [\frac{m v_{1x}^2}{l} + \frac{m v_{2x}^2}{l} + \frac{m v_{3x}^2}{l} + ... + \frac{m v_{Nx}^2}{l}]

or P_x = \frac{m}{l^3} [v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + ... + v_{Nx}^2] \longrightarrow (5)

As: mass of single molecule = m

Also density $\rho = \frac{\text{mass}}{\text{volume}} = \frac{mN}{V}$

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

Putting the value of $\frac{mN}{V}$ in eq. (1) we get:

$$P_x = \frac{\rho}{N} (v_{1x}^2 + v_{2x}^2 + \dots + v_{Nx}^2)$$

or $P_x = \rho \left[\frac{v_{1x}^2 + v_{2x}^2 + \dots + v_{Nx}^2}{N} \right]$

where $\left(\frac{v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2}{N} \right)$ is called mean of squared velocities moving along x direction, known as "mean square" and represented by $\langle v_x^2 \rangle$. Therefore, eq. (6) becomes

$$P_x = \rho \langle v_x^2 \rangle \quad \text{--- (7)}$$

Similarly, pressure on the faces perpendicular to y and z axes will be

$$P_y = \rho \langle v_y^2 \rangle, \quad P_z = \rho \langle v_z^2 \rangle$$

In random motion, the mean square of all the component velocities will be equal.

Hence: $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$

The resultant of all the component velocities is

given as: $\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle$

$$= \langle v_x^2 \rangle + \langle v_x^2 \rangle + \langle v_x^2 \rangle$$

$$= 3\langle v_x^2 \rangle$$

or $\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle$ Thus eq. (7)

becomes $P_x = \frac{\rho}{3} \langle v^2 \rangle \quad \text{--- (8)}$

The above eq. (8) gives the pressure on the face perpendicular to x-axis.

By Pascal's law, the pressure on the other sides and everywhere inside the vessel will be the same provided the gas is of uniform density. so :

$$P_x = P_y = P_z = \frac{F}{3} \langle v^2 \rangle$$

Thus in general :

$$P = \frac{1}{3} F \langle v^2 \rangle \longrightarrow (9)$$

Since : $F = \frac{mN}{V}$

$$\text{Hence : } P = \frac{mN}{3V} \langle v^2 \rangle = \frac{2}{3} \times \frac{N}{V} \langle \frac{1}{2} m v^2 \rangle$$

$$\text{or } P = \frac{2}{3} \frac{N}{V} \langle \frac{1}{2} m v^2 \rangle \longrightarrow (10)$$

$$\text{or } P = \frac{2}{3} N_0 \langle \frac{1}{2} m v^2 \rangle$$

where ' N_0 ' is the no. of molecules per unit volume. Thus :

$$P = \text{constt} \langle K.E \rangle$$

$$\text{or } P \propto \langle K.E \rangle$$

In deriving above eq. only linear motion of molecules is considered. Hence:

"pressure exerted by the gas is directly proportional to the average translational kinetic energy of the gas molecules."

Interpretation of Temperature :-

From the ideal gas law :

$$PV = nRT \longrightarrow (11)$$

where 'n' is the no. of moles of the gas contained in volume 'V' at absolute temp. 'T' and 'R' is called universal gas constant.

Its value is $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ or $8314 \text{ J kmol}^{-1} \text{ K}^{-1}$.

If ' N_A ' is the Avogadro number, then:

$$n = \frac{\text{Total no. of molecules}}{\text{Avogadro number}} = \frac{N}{N_A}, \text{ then}$$

above eq. becomes:

$$PV = \frac{N}{N_A} RT = N \left(\frac{R}{N_A} \right) T$$

$$\text{or } PV = NKT \longrightarrow (12)$$

where ' $k = \frac{R}{N_A}$ ' is called the Boltzmann constt.

$$k = \frac{R}{N_A} = \frac{8.314}{6.02 \times 10^{23}} = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

$$\text{From eq. (12): } P = \frac{N}{V} KT \longrightarrow (13)$$

comparing eq. (10) and (13) we get:

$$\frac{N}{V} KT = \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m v^2 \right\rangle$$

$$\text{or } T = \frac{2}{3K} \left\langle \frac{1}{2} m v^2 \right\rangle \longrightarrow (14)$$

$$\text{or } T = \text{constt} \langle K.E \rangle$$

$$\text{so: } T \propto \langle K.E \rangle$$

This relation shows that "Absolute temp. of an ideal gas is directly proportional to the avg. translational kinetic energy of gas molecules."

Derivation of Gas Laws :-

(i) Boyle's Law :-

From Kinetic theory of gases (Eq. 10), we have:

$$P = \frac{2}{3} \frac{N}{V} \left\langle \frac{1}{2} m v^2 \right\rangle$$

$$\text{or } PV = \frac{2}{3} N \left\langle \frac{1}{2} m v^2 \right\rangle$$

For a given mass ' $N = \text{const.}$ ' If temp. is kept const., then $\langle \text{K.E.} \rangle = \langle \frac{1}{2} m v^2 \rangle = \text{const.}$ so the above eq. is written as:

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

$$\text{or } P \propto \frac{1}{V}$$

Thus pressure ' P ' is inversely proportional to volume ' V ' at const. temperature of the gas which is "Boyle's law".

(ii) Charles's Law :-

From kinetic theory of gases (Eq. 10), we have:

$$P = \frac{2}{3} \frac{N}{V} \langle \frac{1}{2} m v^2 \rangle$$

$$\text{or } V = \frac{2}{3} \frac{N}{P} \langle \frac{1}{2} m v^2 \rangle$$

For a given mass $N = \text{const.}$ If pressure is kept const., then $\frac{N}{P} = \text{const.}$, so above eq.

becomes: $V = \text{const.} \langle \frac{1}{2} m v^2 \rangle$

$$\text{As } \langle \frac{1}{2} m v^2 \rangle \propto T$$

$$\text{Hence } V \propto T.$$

Thus vol. is directly proportional to absolute temp. of the gas if pressure is kept constant, which is known as "Charles's law".

Example 11.1 :- what is the avg. translational K.E. of molecules in a gas at temp. 27°C ?

Sol. :- Given that: $T = 27^\circ\text{C} = 27 + 273 = 300\text{K}$

$$\text{Using the eq. } T = \frac{2}{3k} \langle \text{K.E.} \rangle, \langle \text{K.E.} \rangle = \frac{3}{2} kT$$

$$\therefore \langle \text{K.E.} \rangle = \frac{3}{2} \times 1.38 \times 10^{-23} \times 300 = 6.21 \times 10^{-21} \text{ J.}$$

Example 11.2 :- Find the avg. speed of oxygen molecule in the air at S.T.P.

Sol. :- Given that: $T = 0^\circ\text{C} + 273 = 273\text{K}$, $\langle v \rangle = ?$

Using the eq. $T = \frac{2}{3k} \langle \frac{1}{2} m v^2 \rangle$

$$\text{or } T = \frac{2}{3k} \times \frac{1}{2} m \langle v^2 \rangle = \frac{m}{3k} \langle v^2 \rangle$$

$$\text{or } \langle v^2 \rangle = \frac{3kT}{m}$$

mass of one molecule of $\text{O}_2 = \frac{\text{mass of 1 mole } \text{O}_2}{\text{Avogadro number}}$

$$\text{or } m = \frac{32\text{g}}{6.02 \times 10^{23}} = \frac{32\text{kg}}{6.02 \times 10^{26}}$$

$$\text{or } m = 5.31 \times 10^{-26} \text{kg}$$

$$\therefore \langle v^2 \rangle = \frac{3 \times 1.38 \times 10^{-23} \times 273}{5.31 \times 10^{-26}} = 2.128 \times 10^5 \text{ m}^2/\text{s}^2$$

$$\text{or } \langle v \rangle = 461.35 \text{ m/s}$$

INTERNAL ENERGY :-

(1) Defi. :- "The sum of all forms of molecular energies (kinetic and potential) of a substance is termed as its internal energy."

It is denoted by 'U' and is measured in "joules".

(2) Explanation :- In the study of thermodynamics, usually ideal gas is considered as a working substance. The molecules of an ideal gas are mere mass points which exert no forces on one another. So the internal energy of an ideal gas system is generally the translational K.E. of its molecules. Since the temp. of a system is defined as the avg. K.E. of its molecules, thus for an ideal gas system, the internal energy is directly proportional

to its temperature.

(3) Change in internal Energy :-

The change in internal energy is denoted by ΔU . Since internal energy is directly proportional to temp., so the increase or decrease in temp. of the object is an indication of increase or decrease in its internal energy. ' ΔU ' is taken as +ve when internal energy increases and "-ve" when it decreases.

When a substance is heated, energy associated with its atoms or molecules increases i.e. heat is converted to internal energy.

It is important to note that energy can be added to a system even though no heat transfer takes place. For example, when two objects are rubbed together, their internal energy increases because of mechanical work. Similarly, when an object slides over any surface and comes to rest because of frictional forces, the mechanical work done on or by the system is partially converted into internal energy.

(4) As a state variable :-

In thermodynamics, internal energy is a function of state (or state variable). Consequently, it does not depend on path but depends on initial and final

states of the system.

Consider a system which undergoes a pressure and volume change from (P_a, V_a) to (P_b, V_b) , regardless of the process by which the system changes from initial to state. By expt. it has been seen that the change in internal energy is always the same and is independent of paths C_1 and C_2 as shown in fig-2.

Thus internal energy is similar to the gravitational P.E. So like the P.E. it is change in internal energy and not its absolute value, which is important.

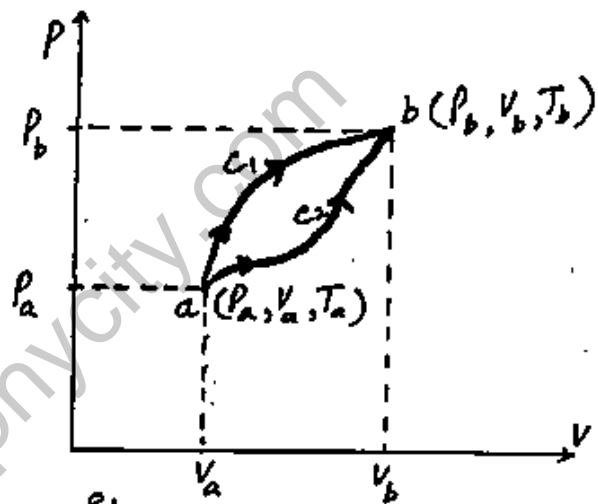


Fig.-2.

WORK AND HEAT :-

Both "heat and work" are similar in transfer of energy by some means. The idea was first applied to the steam engine where it was natural to transfer "heat in" and get "work out". So both "heat in" and "work out" are defined as +ve quantities.

Sign Convention :-

- (i) work done by the system (on its environment) is +ve,
- (ii) " " " on " " (by the " ") " -ve.
- (iii) Heat entering the system +ve and heat leaving

the system '-ve'.

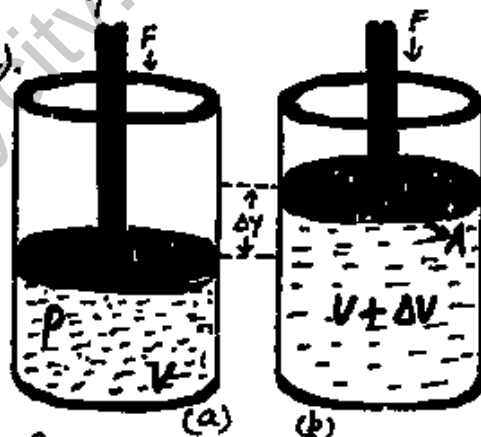
When an amount of heat ' ΔQ ' enters the system, it will appear as either an increase in internal energy or a quantity of work performed by the system on the surrounding or both.

Pressure - Volume Work :-

We can express the work in terms of directly measurable variables such as pressure and volume.

Consider the gas enclosed in the cylinder with a moveable, frictionless piston of cross-sectional area ' A ' as shown in fig.-3(a).

In equilibrium the system occupies volume V , and exerts a pressure ' P ' on the walls of the cylinder and its piston.



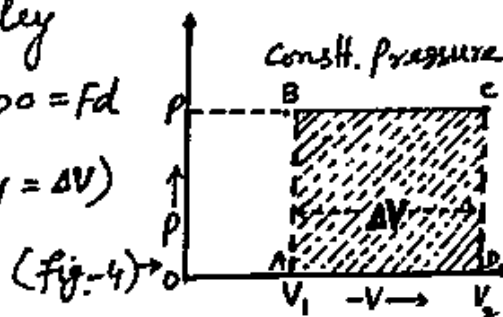
The force ' F ' exerted by the gas on the piston is ' PA '.

We assume that the gas expands through ' ΔV ' very slowly, so that it remains in equilibrium (fig.-3(b)). As the piston moves up through a small distance ' Δy ', the work done by the gas is:

$$\Delta W = \vec{F} \cdot \vec{d} = Fd \cos 0 = Fd$$

$$\text{or } \Delta W = PA \Delta y = P \Delta V \quad (\because A \Delta y = \Delta V)$$

$$\text{Hence } \Delta W = P \Delta V.$$



The work done can be calculated from PV-graph (fig.-4).

LAWS OF THERMODYNAMICS :-

"The general principles which deal with heat energy and its transformation into mechanical energy are called laws of thermodynamics."

FIRST LAW OF THERMODYNAMICS :-

Statement :- "In any thermodynamic process, when heat ' ΔQ ' is added to a system, this energy appears as an increase in the internal energy ' ΔU ' stored in the system plus the work ' ΔW ' done by the system on its surroundings."

Explanation :-

When heat is added to a system, there is an increase in the internal energy due to the rise in temp., an increase in pressure or change in the state. If at the same time, a substance is allowed to do work on its environment by expansion, the heat ' ΔQ ' required will be the heat necessary to change the internal energy of the substance from U_1 in the first state to ' U_2 ' in the second state plus the work ' ΔW ' done on the environment.

$$\text{Thus} \quad \Delta Q = (U_2 - U_1) + \Delta W$$

$$\text{or} \quad \Delta Q = \Delta U + \Delta W \longrightarrow (1)$$

Thus the change in internal energy $\Delta U = U_2 - U_1$

is defined as $\Delta Q - \Delta W$ i.e. $\Delta U = \Delta Q - \Delta W$. Since it is the same for all processes concerning the state, the first law of thermodynamics is observed in heat engines and other devices.

Examples of 1st law :-

(i) A bicycle pump :- A bicycle pump provides a good example of 1st law of thermodynamics. When we pump on the handle rapidly, it becomes hot due to mechanical work done on the gas, raising thereby its internal energy, which is shown, by the increase in temp. of the air. Thus eq. of first law in this case takes the form :

$$-\Delta W = \Delta U - \Delta Q.$$

where : $-\Delta W$ = work done on the system (gas)
 $+\Delta U$ = Increase in internal energy
 $-\Delta Q$ = Heat evolved.

(ii) Human metabolism :-

Human metabolism also provides an example of energy conservation (or first law of thermodynamics), since first law is also known to be another form of law of conservation of energy.

Human beings and other animals do work when they walk, run, or move heavy objects. Work requires energy. Energy is also needed

for growth to make new cells and to replace old cells that have died. Energy transforming processes that occur within an organism are named as metabolism.

We can apply the first law of thermodynamics,

$$\Delta U = \Delta Q - \Delta W$$

to an organism of the human body. Work ' ΔW ' done will result in the decrease in internal energy of the body. Consequently, the body temperature or in other words internal energy is maintained by the food we eat.

Example 11.3 :-

A gas is enclosed in a container fitted with a piston of cross-sectional area 0.1 m^2 . The pressure of the gas is maintained at 8000 N/m^2 . When heat is slowly transferred, the piston is pushed up through a distance of 4 cm . If ' 42 J ' heat is transferred to the system during the expansion, what is the change in internal energy of the system?

Sol. :- Given that: $A = 0.1 \text{ m}^2$, $P = 8000 \text{ N/m}^2$

$$d = \Delta y = 4 \text{ cm} = 0.04 \text{ m}, \quad Q = 42 \text{ J}$$

$$\text{AS } \Delta W = P \Delta V = P A \Delta y$$

$$\Delta U = ?$$

$$\therefore \Delta W = 8000 \times 0.1 \times 0.04 = 32 \text{ J}$$

$$\Rightarrow \Delta U = \Delta Q - \Delta W = 42 - 32 = 10 \text{ J}, \quad \therefore \Delta U = 10 \text{ J}$$

Applications of first law :-

(i) Isothermal process :-

Defi.: "It is a process which is carried out at constant temperature".

Explanation :-

Consider a cylinder fitted with non-conducting walls, non-conducting and frictionless piston and base is conducting. A gas is enclosed in it. It is placed on a heat reservoir, which is a source of large heat capacity, at some temp. T .

This system fulfills the condition for the application of Boyle's law. Therefore, when gas expands or compresses isothermally, the product of its pressure and volume during the process remains constant. If P_1, V_1 are initial pressure and volume where as P_2, V_2 are pressure and volume after the isothermal change take place (Fig.-6),

then : $P_1 V_1 = P_2 V_2$

In case of an ideal gas, the P.E. associated with its molecules is zero, hence the internal energy of an ideal gas depends only on

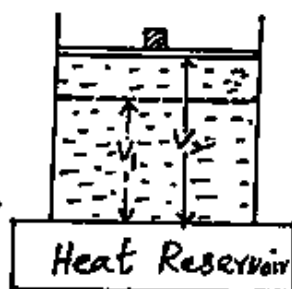


Fig.-5.

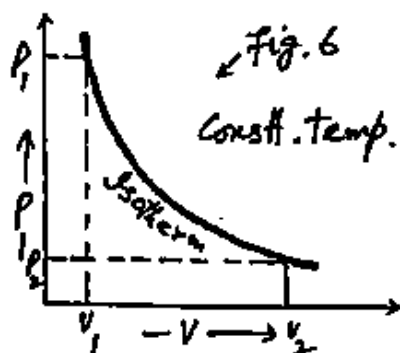


Fig. 6

Const. Temp.

its Temp., which in this case is constant, therefore, $\Delta U = 0$. Hence, the first law of thermodynamics reduces to:

(i) $\Delta Q = \Delta W$ (Isothermal expansion).

Also: (ii) $-\Delta Q = -\Delta W$ (Isothermal compression)

Here, case (i) shows that gas expands and does external work ' ΔW ', it requires an amount of heat ' ΔQ ' to be supplied to the gas in order to produce an isothermal change. on the other hand case (ii) shows that the gas is compressed isothermally, ' $-\Delta W$ ' is the work done on the gas and ' $-\Delta Q$ ' heat flows out of the gas.

Since transfer of heat from one place to another requires time, hence, to keep the temp. of the gas constant, the expansion or compression must take place slowly.

The curve representing an isothermal process is called an isotherm (fig-6).

(ii) Adiabatic Process :-

Defi. :- "An adiabatic process is the one in which no heat enters or leaves the system".

Explanation :-

For an adiabatic process the prevention of heat flow may be done either by surrounding the system with a thick layer of heat-

insulating material (such as cork, asbestos, styrofoam etc.), or by performing the process quickly. Since the flow of heat requires finite time, so any process performed quickly enough will be practically adiabatic.

Adiabatic change occurs when the gas expands or is compressed rapidly. The examples of adiabatic process are:

- (i) The rapid escape of air from a burst tyre.
- (ii) Passage of sound through air
- (iii) Cloud formation in the atmosphere

There are two types of adiabatic process. As seen from the formula: $\Delta Q = \Delta U + \Delta W$, under the condition ' $\Delta Q = 0$ ', we have:

$$0 = \Delta U + \Delta W$$

$$(1) \quad \Delta W = -\Delta U \quad (\text{Adiabatic expansion})$$

$$(2) \quad \Delta U = -\Delta W \quad (\text{" " Compression}).$$

Case (1) shows that if the gas expands and does work, it is done at the cost of internal energy of its molecules and, hence, temp. of the gas falls, and the process is called "adiabatic expansion".

Case (2) shows that if the gas is compressed, work is done on it and as a result temp. of gas rises due to increase in internal energy.

of gas molecules. This process is called "adiabatic Compression".

As the temp. of the gas does not remain constant, so it has been seen that:

$$pV^\gamma = \text{constant}$$

where: $\gamma = \frac{C_p}{C_v} = \frac{\text{Molar specific heat at const. Pressure}}{\text{Molar specific heat at const. Volume}}$

The curve representing an adiabatic process is called an "adiabat" (fig-7). A comparison of an "isotherm" and "adiabat" is also shown in this fig.

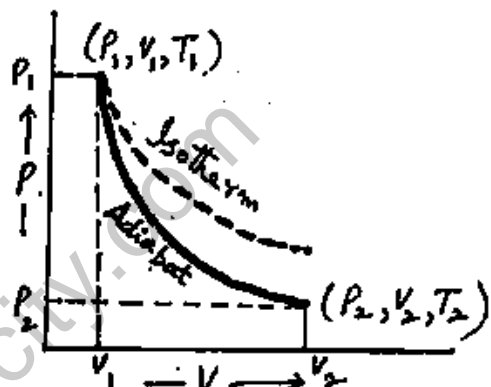


fig-7. Adiabatic and Isotherm

Let at the initial stage the values of P, V, T for "isotherm" and "adiabat" are same. If we expand the gas to the same final volume, the values of ' P ' and ' T ' in case of adiabat are less than the values of ' P ' and ' T ' of the gas expanded isothermally. The reason being the non-availability of heat in adiabatic change. That is why the adiabat is steeper than isotherm.

MOLAR SPECIFIC HEATS OF A GAS

Molar Specific heat :-

"It is the amount of heat required to raise the temp. of one mole of the substance through 1K."

To study the effect of heating the gases, either pressure or volume is kept constant.

So we begin the topic with definitions of the molar specific heats of a gas in two ways:

(i) Molar specific heat at constant volume:

"It is the amount of heat transfer required to raise the temp. of one mole of the gas through '1K' at constant volume."

It is denoted by C_v . Its unit is $\text{J mol}^{-1} \text{K}^{-1}$

Heating Under Const. Volume:

Consider a cylinder fitted with non-conducting walls, non-conducting and frictionless piston.

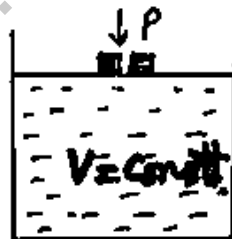


Fig-8.

If one mole of an ideal gas is heated in it at constant volume, so that its temperature rises by ' ΔT ', then the heat transferred ' ΔQ_v ' is given by:

$$\Delta Q_v = (1) C_v \Delta T \quad (\because n = 1 \text{ mole})$$

$$\text{or} \quad \Delta Q_v = C_v \Delta T \longrightarrow (1)$$

Because $V = \text{const}$, or $dV = 0$, so no work is done ($\Delta W = 0$), as shown in fig-8. Applying first law of thermodynamics:

$$\Delta Q_v = \Delta U + \Delta W$$

$$\text{or} \quad \Delta Q_v = \Delta U \longrightarrow (2) \quad (\because \Delta W = 0)$$

Comparing eq. (1) and (2), we get:

$$\Delta U = C_v \Delta T \longrightarrow (3)$$

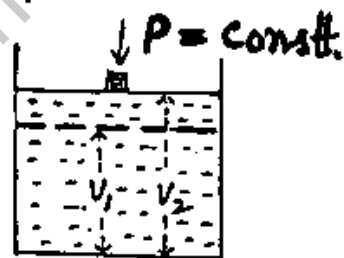
(ii) Molar specific heat at const. pressure :-

"It is the amount of heat transfer required to raise the temp. of one mole of the gas through '1K' at constant pressure."

It is denoted by ' C_p ' and has units of $J \text{ mol}^{-1} \text{ K}^{-1}$.

Heating Under Const. Pressure :-

Now, let us heat the same system under constant pressure.



To raise the temp. of one mole of the gas by ' ΔT ' at constant pressure, the heat transfer ΔQ_p is given by: fig.-9.

$$\Delta Q_p = (1) C_p \Delta T \quad (\because n = 1 \text{ mole})$$

$$\text{or} \quad \Delta Q_p = C_p \Delta T \longrightarrow (4)$$

Derivation of $C_p - C_v = R$:-

When one mole of a gas is heated at constant pressure, the internal energy increases by the same amount as at constant volume for the same rise in temperature ' ΔT '. Thus as in eq. (3) we have:

$$\Delta U = C_v \Delta T \longrightarrow (3')$$

Since the gas expands to keep the pressure constant, so it does work ' ΔW ' given by:

$$\Delta W = P \Delta V \longrightarrow (5)$$

where ' ΔV ' is the increase in volume. From first law we have:

$$\Delta Q_p = \Delta U + \Delta W \longrightarrow (6)$$

Putting values from eq. (3) and (5) in eq. (6) we get:

$$\Delta Q_p = C_v \Delta T + P \Delta V \longrightarrow (7)$$

For one mole of an ideal gas, the eq. of state is written as:

$$PV = (1)RT \quad (n = 1 \text{ mole})$$

$$\text{or} \quad PV = RT \longrightarrow (8)$$

At constant pressure P , amount of work done by one mole of a gas due to expansion ' ΔV ' (fig.-9) caused by the rise in temperature ' ΔT ' is given by:

$$P \Delta V = R \Delta T \longrightarrow (9)$$

Putting the above value in eq. (7) we have:

$$\Delta Q_p = C_v \Delta T + R \Delta T \longrightarrow (10)$$

Now comparing eq. (4) and (10) we get:

$$C_p \Delta T = C_v \Delta T + R \Delta T$$

$$\text{or} \quad C_p = C_v + R$$

$$\text{or} \quad C_p - C_v = R.$$

It is clear from above eq. that $C_p > C_v$ by an amount equal to universal gas constant ' R '.

REVERSIBLE AND IRREVERSIBLE PROCESSES :

(i) Reversible Process :- "A reversible process is the one which can be retraced in exactly reverse order, without producing any change in the surroundings."

In the reverse process, the working substance passes through the same stages as in the direct process but thermal and mechanical effects at each stage are exactly reversed. If heat is absorbed in the direct process, it will be given out in the reverse process. If work is done by the substance in the direct process, work will be done on the substance in the reverse process. Hence, the working substance is restored to its original conditions.

Reversible cycle :-

"A succession of events which bring the system back to its initial condition is called a cycle. A reversible cycle is the one in which all the changes are reversible."

Examples :- Although no actual change is completely reversible but following processes are approximately or conditionally reversible:

(a) Compression and expansion of a substance

performed slowly.

(b) Slow compression of gas in a cylinder.

(c) Melting of ice into water and freezing of water into ice at 0°C .

(ii) Irreversible Process:-

"If a process can not be retraced in the backward direction by reversing the controlling factors, it is an irreversible process."

All changes which occur suddenly or which involve friction or dissipation of energy through conduction, convection or radiation are irreversible.

Examples:- (a) An explosion is a highly irreversible process (b) work done against friction. (c) All the engines of practical life are irreversible.

HEAT ENGINE :-

(i) Definition :- "A device which converts heat energy into mechanical work is called a heat engine."

(ii) Principle :- A heat engine works in a cycle.

*- As conversion of heat into work causes a drop in temp. of working substance, so a heat engine is made cyclic to provide a continuous supply of work.

(iii) Construction :- Basically a heat engine

Consists of following three components:

- (i) A hot reservoir or source, usually named as 'HTR' (high temp. reservoir), which can supply heat at high temperature.
- (ii) A cold reservoir or sink, usually named as 'LTR' (low temp. reservoir), into which heat is rejected at low temperature.
- (iii) A working substance, usually a gas, which can absorb heat from source, convert some of it into work and rejects the remaining heat to sink.

(IV) Diagram:- The heat engine is represented by the block diagram (fig.-10).

(V) Working (or operation):-

The heat engine absorbs a quantity of heat ' Q_1 ' from the heat source (HTR) at temp. ' T_1 '. It does work ' ΔW ' and expels heat ' Q_2 ' to 'LTR' (sink) at temp. T_2 . As working substance goes through a cyclic process, in which the substance eventually returns to its initial state, the

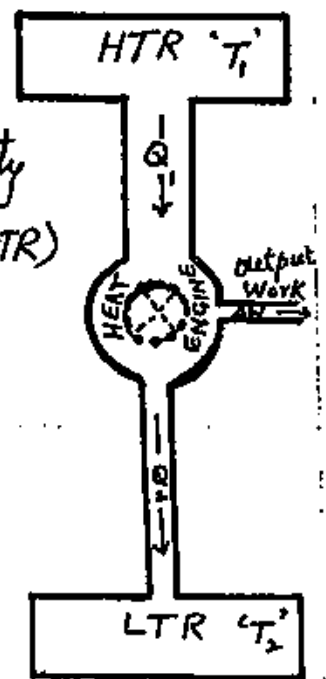


fig.-10. A heat engine

change in internal energy is zero ($\Delta U = 0$).

Hence from the first law of thermodynamics, net work done should be equal to the net

heat absorbed i.e. $\Delta Q = \Delta U + \Delta W$

$$\Delta W = Q_1 - Q_2 \quad (\because \Delta U = 0)$$

(VI) Efficiency:- The efficiency of a heat engine is denoted by ' η ' and is defined as:

$$\eta = \frac{\text{output}}{\text{input}} = \frac{\Delta W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\text{or } \eta = 1 - \frac{Q_2}{Q_1} \quad \text{or } \% \eta = \left(1 - \frac{Q_2}{Q_1}\right) \times 100$$

In practice, the petrol engine of a motor car extracts heat from the burning fuel and converts a fraction of this energy into work and expels the rest to the atmosphere (sink). It has been observed that the efficiency of petrol engine is approximately 25% and that of diesel engines is about 35 to 40%.

SECOND LAW OF THERMODYNAMICS :-

First law of thermodynamics tells us that heat energy can be converted into equivalent amount of work, but it is silent about the conditions under which this conversion takes place. The second law is concerned with the circumstances in which heat can be converted into work and direction of flow of heat.

Second law of thermodynamics can be stated in a no. of different ways.

According to Lord Kelvin's statement, which

is based on the working of a heat engine, the second law is defined as:

"It is impossible to devise a process which may convert heat, extracted from a single reservoir, entirely into work without leaving any change in the working system."

This means that a single heat reservoir, no matter how much energy it contains, can not be made to perform any work. This law demands that "the two bodies at different temperatures are essential for the conversion of heat into work. Hence for the working of heat engine there must be a source of heat at a high temp. and a sink at low temp. to which heat may be expelled. The reason for our inability to utilize the large amount of heat contents of oceans and atmosphere is that there is no reservoir at a temperature lower than any one of the two.

Another statement, which is called Clausius's statement is given below:

"It is impossible to cause heat to flow from a cold body to a hot body without the expenditure of external work (or energy)."

CARNOT ENGINE AND CARNOT'S

THEOREM :

(i) CARNOT ENGINE :-

Sadi Carnot in 1840 described an ideal heat engine, free from friction and heat losses. It has maximum possible efficiency, that can be obtained by any heat engine operating in a cycle between two given reservoirs, but is less than 100%. Its power is nil and can't be put to practical use. It serves only as a model to compare efficiencies of real heat engines.

(ii) PRINCIPLE :- It works on the principle of any cyclic heat engine and its cycle is called "Carnot cycle".

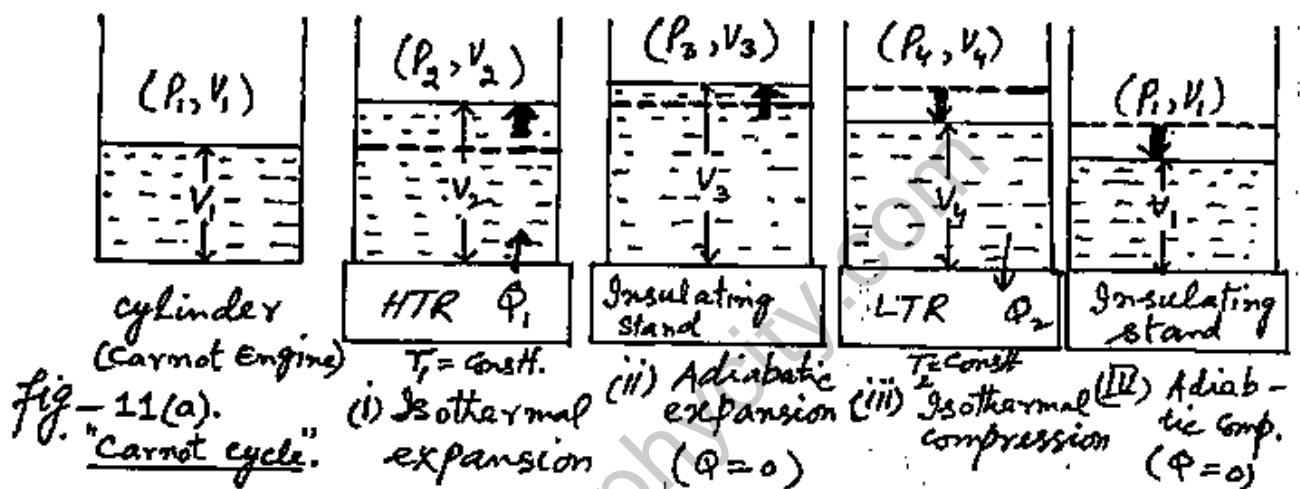
(iii) CONSTRUCTION :- It consists of a cylinder filled with a non-conducting walls, non-conducting and frictionless piston and conducting base. An ideal gas is used as working substance. Two heat reservoirs i.e. 'HTR' at temp. T_1 and 'LTR' at temp. T_2 act as source and sink respectively. An insulating stand is also used for adiabatic changes.

(iv) WORKING :- The operating cycle of Carnot engine is called Carnot cycle. A Carnot cycle.

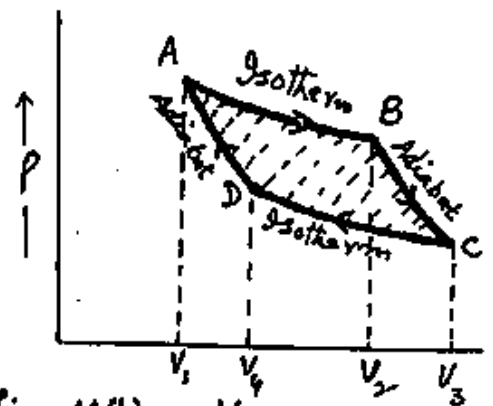
using an ideal gas as a working substance is shown in fig- along with its "PV-diagram".

It consists of following four steps.

(a) The gas is allowed to expand isothermally at temp. T_1 , absorbing heat Q_1 from the hot reservoir. The process is represented by curve 'AB'.



(b) The gas is then allowed to expand adiabatically until its temp. drops to T_2 . The process is represented by curve 'BC'.



(c) The gas at this stage is compressed isothermally at temp. T_2 rejecting heat Q_2 to the cold reservoir. The process is represented by curve 'CD'.

(d) Finally the gas is compressed adiabatically to restore its initial state at temp. T_1 . The process is represented by curve 'DA'.

Thermal and mechanical equilibrium is maintained all the time so that each process is perfectly reversible. As the working substance returns to the initial state, there is no change in its internal energy i.e. $\Delta U = 0$.

The net work done during one cycle equals to the area enclosed by the path ABCDA of the pV-diagram. It can also be estimated from net heat ' ΔQ ' absorbed in one cycle i.e. $\Delta Q = Q_1 - Q_2$.

From 1st law of thermodynamics:

$$\Delta Q = \Delta U + \Delta W$$

$$\text{or } \Delta Q = \Delta W \quad (\because \Delta U = 0)$$

$$\text{or } \Delta W = Q_1 - Q_2 \longrightarrow (1)$$

EFFICIENCY :- The efficiency ' η ' of the heat engine is defined as:

$$\eta = \frac{\text{output (work)}}{\text{Input (Energy)}}$$

$$\text{Thus: } \eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$\text{or } \eta = 1 - \frac{Q_2}{Q_1} \longrightarrow (2)$$

As the energy transfer in an isothermal or compression turns out to be proportional to Kelvin temperature, so ' Q_1 ' and ' Q_2 ' are proportional to Kelvin temperatures ' T_1 ' and ' T_2 ' respectively,

$$\text{Hence: } \eta = 1 - \frac{T_2}{T_1} \longrightarrow (3)$$

The efficiency is usually taken in percentage (%), so in that case:

$$\text{percentage efficiency} = \left(1 - \frac{T_2}{T_1}\right) \times 100$$

$$\text{or } \%(\eta) = \left(1 - \frac{T_2}{T_1}\right) \times 100 \rightarrow (4).$$

Thus the efficiency of Carnot engine depends on the temp. of hot and cold reservoirs. It is independent of the nature of working substance. The larger the temp. difference of two reservoirs, the greater is the efficiency. But it can never be 100% or one unless cold reservoir is at absolute zero temp. ($T_2 = 0K$). Such reservoirs are not available and hence the max. efficiency is always less than one.

In most practical cases, the cold reservoir is near room temp., so the efficiency can only be increased by raising the temp. of the hot reservoir. All real heat engines are less efficient than Carnot engine due to friction and other heat losses.

CARNOT'S THEOREM :- The Carnot cycle establishes an upper limit on the efficiency of all heat engines. No practical heat engine can be perfectly reversible and also energy dissipation is inevitable. This fact is stated in "Carnot theorem":

(1). No heat engine can be more efficient than

a Carnot engine operating between the same two temperatures. Also:

(2) All Carnot's engines operating between the same two temperatures have the same efficiency, irrespective of the nature of working substance.

Example 11.4 :- The turbine in a steam power plant takes steam from a boiler at 427°C and exhausts into a low temp. reservoir at 77°C .

What is the max. possible efficiency?

Sol. :- Given that: $T_1 = 427^{\circ}\text{C} + 273 = 700\text{K}$

$$T_2 = 77 + 273 = 350\text{K}$$

using formula: $\eta = \left(1 - \frac{350}{700}\right) \times 100 = 50\%$

or $\eta = 50\%$

THERMODYNAMIC SCALE OF TEMPERATURE

A temperature scale is established by two fixed points using certain physical properties of a material (e.g. mercury), which varies linearly with temperature. The Carnot cycle provides us the basis to define a temp. scale that is independent of material properties. According to it, the ratio $\frac{Q_2}{Q_1}$ depends only on the temp. of two heat reservoirs. The ratio of the two temps. $\frac{T_2}{T_1}$ can be found by operating a reversible Carnot cycle between these two temps. and carefully measuring the heat transfers Q_2 and Q_1 .

DEFINITION :- "The thermodynamic scale of temp. is defined by choosing 273.16 K as the absolute temp. of the tripple pt. of water as one fixed point and absolute zero, as the other."

The unit of thermodynamic scale is Kelvin.

KELVIN :- "one Kelvin (1 K) is defined as $\frac{1}{273.16}$ of the thermodynamic temp. of the tripple point of water."

The tripple pt. is a state in which ice, water and vapour coexists in equilibrium and it occurs uniquely at one particular pressure and temperature. If heat ' Q ' is absorbed or rejected by the system at corresponding temp. ' T ' when the system is taken through a Carnot cycle and Q_3 is the heat absorbed or rejected by the system when it is at the temperature of tripple point of water, then unknown temperature ' T ' in Kelvin is given by:

$$T = 273.16 \frac{Q}{Q_3}$$

Since this scale is independent of the working substance, hence, can be applied at very low temperature.

PETROL ENGINE :-

Although different engines may differ in their construction technology but they are based on the principle of a Carnot cycle. A typical four stroke petrol engine (fig.-12) also undergoes four successive processes in each cycle.

(1) The cycle starts on the intake stroke in which piston moves outward and petrol air mixture is drawn through an inlet valve into the cylinder from the carburetor at atmospheric pressure.

(2) on the Compression Stroke, the inlet valve is closed and the mixture is compressed adiabatically by inward movement of the piston.

(3) on the Power Stroke, a spark fires the mixture causing a rapid increase in pressure and temperature. The burning mixture expands adiabatically and forces the piston to move outward. This is the stroke which delivers power to crank shaft to drive the flywheels.

(4) on the exhaust stroke, the outlet valves open.

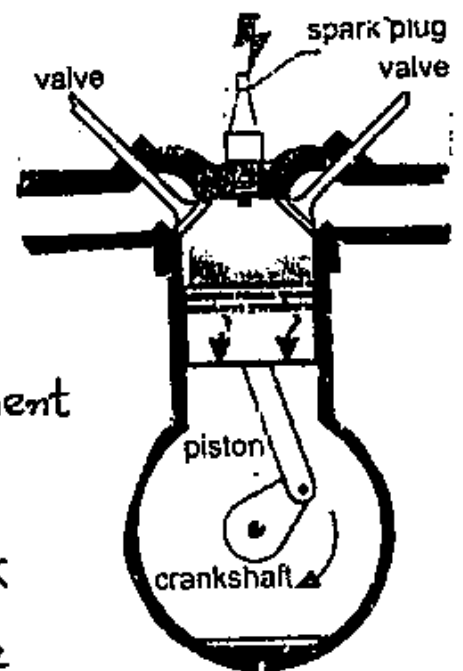


fig-12(a). A petrol engine

The residual gases are expelled and piston moves inward.

The cycle then begins again. Most motorbikes have one cylinder engine but cars usually have four cylinders on the same crankshaft, as shown in fig.-12(b).

The cylinders are timed to fire turn by turn in succession for a smooth running of the car. The actual efficiency of properly tuned engine is usually not more than 25% to 30%

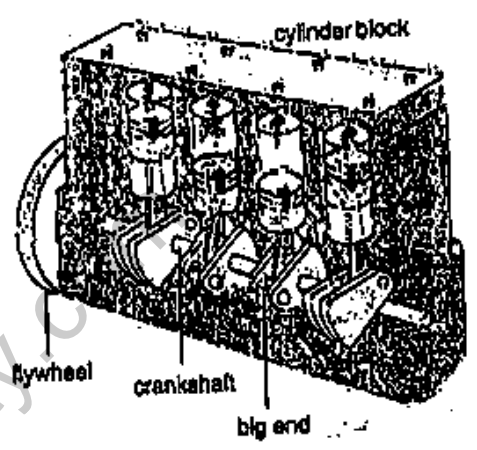


fig.-12(b) Petrol engine of a car.

because of friction and other heat losses.

DIESEL ENGINE :-

No spark plug is needed in the diesel engine (fig.-13). Diesel is sprayed into the cylinder at max. compression. Because air is at very high temp. immediately after compression, the fuel mixture ignites on contact with air in the cylinder and pushes the piston outward. The efficiency of diesel engine is about 35% to 40%.

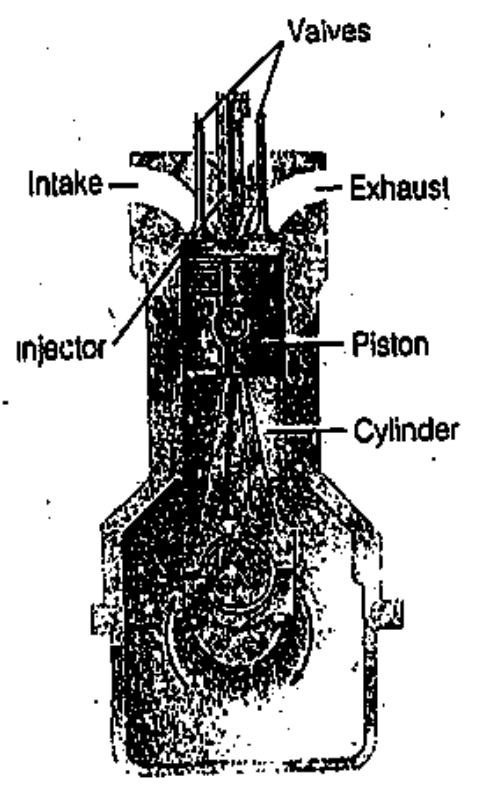


fig.-13. A diesel Engine.

ENTROPY :-

(1) Introduction :- The concept of entropy was introduced in thermodynamics by R. Clausius in 1856. It provides another variable to describe the state of a system along with P, V, T and internal energy.

(2) Definitions :- (i) Entropy is a measure of disorder of a system.

(ii) Entropy is the measure of unavailability of energy.

(3) Measurement of entropy :-

If a system undergoes a reversible process during which it absorbs a quantity of heat ' ΔQ ' at absolute temp. ' T ', then the increase in the state variable called entropy (S) of a system is given by:

$$\Delta S = \frac{\Delta Q}{T} \longrightarrow (1)$$

Like P.E. or internal energy, it is the change in entropy of the system which is important. ' ΔS ' is '+ve', when heat is added and '-ve' when heat is removed from the system. The unit of entropy is J/K .

(4) Change in entropy :-

As said earlier, it is change in entropy that is important and measurable quantity as compared to its absolute value. For this purpose, suppose

an amount of heat ' Q ' flows from a reservoir at temp. ' T_1 ' through a conducting rod to a reservoir at temp. ' T_2 ' when $T_1 > T_2$. The change in entropy of the reservoir, at temp T_1 , which loses heat, decreases by ' $\frac{Q}{T_1}$ ' and of the reservoir at temp. T_2 , which gains heat, increases by ' $\frac{Q}{T_2}$ '. As $T_1 > T_2$ so $\frac{Q}{T_2}$ will be greater than ' $\frac{Q}{T_1}$ ' i.e. $\frac{Q}{T_2} > \frac{Q}{T_1}$. Hence, net change in entropy is:

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1} = Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

or $\Delta S = Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ is +ve.

It follows that in all natural processes where heat flows from one system to another, there is always a net increase in entropy.

(5) Second law of thermodynamics in terms of entropy :- According to this law:

"If a system undergoes a natural process, it will go in the direction that causes the entropy of the system plus the environment to increase."

(6) Entropy and Molecular disorder :-

It is observed that a natural process tends to proceed towards a state of greater disorder. Thus, there is a relation between entropy and molecular disorder. For example, an irreversible

heat flow from a hot to a cold substance of a system increases disorder because the molecules are initially sorted out in hotter and colder regions. This order is lost when the system comes to thermal equilibrium. Addition of heat to a system increases its disorder because of increase in avg. molecular motion. Similarly, free expansion of gas increases its disorder because the molecules have greater randomness of position after expansion than before. Thus in both examples, disorder and hence, entropy is said to be increased.

We can conclude that only those processes are probable for which entropy of the system increases or remains constant. The process for which entropy remains constant is a reversible process; whereas for all irreversible processes, entropy of the system increases.

(7) Degradation of energy :-

Every time entropy increases, the opportunity to convert some heat into work is lost. For example, there is an increase in entropy when hot and cold waters are mixed. The heat energy after mixing is no longer available and can't be converted into work. Therefore, increase in entropy

means degradation of energy from a higher level where more work can be extracted to a lower level at which less or no work can be done i.e. it is degraded, from more orderly form to less orderly form.

In all real processes where heat transfer occurs, the energy available decreases or entropy increases. Even if the temp. of a system decreases, thereby decreasing the entropy, it is at the expense of net increase in entropy for some other system. When all the systems are taken together as the universe, the entropy of the universe always increases.

Example 11.7 :- Calculate the entropy change when 1.0 kg of ice at 0°C melts into water at 0°C . Latent heat of fusion of ice $L_f = 3.36 \times 10^5 \text{ J kg}^{-1}$.

Sol. :- Given that :- $m = 1 \text{ kg}$, $T = 0^\circ\text{C} + 273 = 273 \text{ K}$,

$$L_f = 3.36 \times 10^5 \text{ J/kg}.$$

We know that : $\Delta S = \frac{\Delta Q}{T} = \frac{mL_f}{T}$ ($\because \Delta Q = mL_f$)

or $\Delta S = \frac{1 \times 3.36 \times 10^5}{273} = 1.23 \times 10^3 \text{ JK}^{-1}$.

$\therefore \Delta S = 1.23 \times 10^3 \text{ JK}^{-1}$.

Thus entropy increases as ice changes into water which is actually a measure of increase in disorder of water molecules.

ENVIRONMENTAL CRISIS AS ENTROPY CRISIS:

The second law of thermodynamics provides us the key for both understanding our environmental crisis, and for understanding how we must deal with this crisis.

From a human standpoint, the environmental crisis results from our attempts to order the nature for our comforts and greed. From a physical standpoint, however, the environmental crisis is an entropy or disorder crisis. An attempt to increase the order of a system will produce an even greater increase in entropy or disorder in the environment.

The energy processes we use are not very efficient. As a result most of the energy is lost as heat to environment. Although we can improve the efficiency but 2nd law imposes an upper limit on efficiency improvement. Thermal pollution is an inevitable consequence of 2nd law of thermodynamics. The increase in thermal pollution of the environment means increase in the entropy.

In addition to thermal pollution, the most energy transformation processes such as heat engines used for transportation and for power generation

cause air pollution. In effect, all forms of energy production have some undesirable effects.

The imperative from thermodynamics is that whenever you do anything, be sure to take into account its present and possible future impact on your environment.

QUESTIONS :

The answers to the questions at the end of the chapter are given below:

Q. 11.1 :- The no. of molecules in a gas is large and their motion is random. The no. of molecules moving in any direction with certain velocity is equal to the no. of molecules moving in opposite direction with the same velocity. The avg. velocity of the molecules is, therefore, zero. Let ' v_x ' be the velocity of a molecule along +x-axis. Then after collision its velocity will be ' $-v_x$ '. So

$$\langle v \rangle = \frac{(v_x) + (-v_x)}{2} = 0$$

Hence motion of molecules is not justified. In such cases, avg. of squared velocities is taken which will not be zero. So

$$\langle v^2 \rangle = \frac{(v_x)^2 + (-v_x)^2}{2} \neq 0.$$