CHAPTER 3

THERMODYNAMICS – I

3.1 Introduction :

The living universe with all its belongings is the manifestation of the absolute truth, being full of harmony in its each breath. Religious minded people have the faith that behind such beautiful, truthful manifestation and absolute harmony, exists the supreme authority. The materialists visualise all the manifestations in nature as the outcome of many ageold interactions following certain definite rules and laws. Whatever may be the way of defining the nature it is a fact that everything occuring in nature is full of harmony whether it is the rushing of stream down the hill, giagantic eruption of volcanos, formation of delta, evolution of organic species or the blooming of colourful world of flowers–although somewhere it may be apparently found to be anharmonic. The natural processes proceed smoothly, spontaneously at a rate moderate or extremely slow or fast, maintaining a perfect balance in its occurrence without having a least chance to be reversed as if the entire universe as a whole is rushing towards the ultimate equilibrium state of eternity.

Through time immemorial keen observation to the events of nature and from the everday experience men came to know that all these on the macroscopic scale are due to different modes of intraction of matter with energy and the interconvertibility of different forms of energy, which in the microscopic scale originate from interaction among atoms, molecules and subatomic particles. All these interactions have given birth consciousness to a huge ordered collection of atoms and molecules in the name of life. Large many a scientists through tireless devotion over a century established basic laws regarding energetics, known as laws of thermodynamics, only through experience. Classical thermodynamics is that branch of science which by its very name indicates the science relating to the dynamic nature of heat. It considers the study of the systems under equilibrium condition and not in progress. It also considers the interconvertibility of different forms of energy and mainly heat into work and vice versa. The laws of thermodynamics are very simple and are applicable only to the macroscopic world, e.g. in case of few grams of ice and not in the microscopic world i.e., in case of few molecules or atoms although the first law is applicable even in case of microscopic system. The application does not require any knowledge about the structure of matter.

Instead of high grade mathematics what is required to make the subject easily understandable is keen logical approach. Apparently the subject appears to be abstract being a collection of simple equations but careful systematic logical study of the physical significance lying behind the useful relations and equations and their simultaneous applications in explaining the occurrence of many events in nature makes the subject interesting. With the help of laws of thermodynamics it is possible to predict the possibility and direction of occurrence of a macroscopic process under a given set of conditions and also the extent of advancement. Thermodynamics does not

143

produce any information regarding the rate of the process. Unlike classical thermodynamics; statistical thermodynamics considers the contribution of each molecule towards the bulk property and takes into a account the structure of matter. Irreversible thermodynamics on the other hand considers the process in progress. The present study is confined only to classical thermodynamics and its applications.

A thorough understanding of thermodynamics is essential to understand clearly homogeneous and heterogeneous equilibria, ionic equilibria, behaviours of solution, electrochemistry, surface chemistry, biochemical process and bioenergetics too. It has immense application in metallurgy and in many industrial process (i) in converting the dissipated form of energy into useful form namely electrical energy and work, (ii) in transferring heat from lower to higher temperature, (iii) in converting sea water into drinking water by desalination etc. In general thermodynamics provides an easiest path to understand the qualititative and quantitative aspects of many spontaneous and non-spontaneous physical or chemical processes and is applicable to a system present at equilibrium or nearly at equilibrium condition.

3.2 Fundamental Terms used in Thermodynamics :

Before going into the details of thermodynamics a student must have a clear sense about the common terms frequently used in thermodynamics.

3.2.1 System :

In our everyday life whenever we define, describe or discuss about something, in reality or in our imaginary sphere we must have the subject of discussion on which our entire attention is focussed. The subject of discussion may be the universe as a whole or a portion of it and is defined as the system, e.g., when we discuss about the problems of our society, the society becomes the system. When we tell something about human body in general, human body becomes the system. Similarly in thermodynamics too, system is defined as that part of the universe whose thermodynamic properties are under consideration. Thermodynamic system may be homogeneous or heterogeneous or may be an evacuated space full of radiation. When we are focussing our attention to a portion of the universe to understand its behaviour that portion, called system, must be separated from the remaining portion of the universe by means of boundary. The boundary may be real or imaginary but its presence must be considered. When we are studying the behaviour of an ideal gas confined in a cylinder, the wall of the cylinder acts as the boundary and hence it is a real boundary, whereas the boundaries of cloud, flame, smoke issuing from chimney, spherical illuminated zone surrounding a glowing bulb, the atmosphere and the liquid-vapour interface are all imaginary.

3.2.2 Surroundings :

The portion of the universe apart from the system, which intracts with the system is commonly called surroundings. The terms universe and surroundings need more clarification than the term system. Universe in thermodynamic sense bears a quite different notion than the usual

meaning of that term. In thermodynamic sense surroundings means that portion of the material world enclosing the system, upto which a change occurring in the system has it influence, e.g. burning of a lamp produces heat and light and affects the environment in two ways. If the effect of light is only considered, then the space enclosing the lamp, which is elluminated by the light, is called the surroundings. On the other hand if the effect of produced heat is only considered, then obviously a narrow space affected by the produced heat, is called the surroundings.

3.2.3 Universe :

System and the surroundings together constitute the Universe.

So, to consider universe in thermodynamic sence one must have to consider —

(i) the depth of the change occurring in the system

(ii) the ways by which system interacts with its environment due to the change occurring in it and

(iii) the intensity of the effect produced in the environment.

When ice cubes are added to a large quantity water taken in a container at room temperature, ice melts and the temperature of water decreases. Here ice is the system and water behaves as surroundings when the melting of ice is considered and both constitute the universe. When the point of consideration is the cooling of a certain amount of water by placing the beaker containing water into ice cubes, water acts as the system and ice acts as the surroundings. When ice water mixture is taken in a thermoflask the resultant mixture as a whole may be considered as the system and surroundings is absent here since the mixture as a whole exchanges neither energy nor the matter with any portion outside the system. So to consider system, surroundings and universe one must have logical sense regarding the notion of the change considered. Moreover surroundings is usually considered as a large heat reservoir.

The boundary (real) of the system is called **diathermal** if it allows the migration of heat from system to surroundings and vice versa, and when it does not do so, it is called **adiabatic**.

3.2.4 Classification of system :

Depending upon the nature of the boundary the sytem interacts in different ways with the surroundings regarding the exchange of energy and matter. Accordingly the system is classified as open, closed and isolated system.

◆ Open System

An open system is one which exchanges both energy and matter with the surroundings and is always in close contact with the surroundings. Due to close intimacy of the system with the surroundings, any change occurring in the system will influence the surroundings and the surroundings will behave accordingly. Every living being in nature is an open system. We take food from the surrdoundings and excrete waste materials to it and also exchange heat. Even a cell or a muscle within a living being is also an open system. Vapourisation of water taken in an open container is also an example of an open system. As open system can exchange mass and energy with the surroundings, during any process its energy does not remain conserved.

Phy Chem–19

◆ Closed System

A closed system is one which exchanges energy but not the matter with the surroundings, i.e., in a closed system the relation with the surroundings is more restricted than that is present in an open system, A system separated by diathermal wall from the surroundings behaves as a closed system, e.g. ice taken in a closed glass container behaves as a closed system since placing of the container at room temperature will cause the ice to melt keeping its mass unchanged. Sealed bottle of cold drinks, well packed food materials are examples of closed system.

◆ *Isolated System*

An isolated system is one which does not exchange energy and matter with the surroundings i.e., an isolated system is one which is totally cut off from the contact of surroundings in respects of energy and matter exchange. A system separated by fixed adiabatic wall from the surroundings behaves as an isolated system. A perfect isolated system is an abstract concept since no wall is perfectly adiabatic. Liquid taken in a thermoflask approximates to an isolated system since matter exchange is totally prevented but heat exchange with the surroundings can not prevented completely. If any change occurs in an isolated system no effect is produced in the surroundings.

3.2.5 Process :

A process occurring in the system is said to be **isothermal** when the temperature of the system remains constant during the process, e.g., boiling of water under 1 atm pressure occurs at 100^0C and hence the process is called an isothermal process.

A process occurring in the system is said to be **adiabatic** only when the system at each step of the process does not exchange heat with the surroundings. If in a process it is observed that the overall heat change is zero due to absorption and release of same quantity of heat at the successive steps, the process can not be stated as adiabatic although the condition $Q = 0$ is maintained for the overall process. Regelation of ice is associated with successive absorption and expulsion of heat by that portion of ice which undergoes regelation so that overall heat change is zero.

Moreover to carryout an adiabatic process the system must not always be kept isolated from the surroundings by adiabatic wall. Even in an open system or in a closed system an adiabatic process may occur provided the change of the system occurs so fast that the system finds no time to exchange heat with the surroundings and hence the process becomes adiabatic, e.g., sudden lowering of pressure of a gas is associated with a lowering of temperature since the gas molecules do not find adequate time to absorb the required heat from surroundings for expansion. The combustion of fuel occurs so fast that the heat produced during combustion is absorbed by the products of combustion and the unreacted reactants instead of being migrated to the surroundings. The heated gaseous products form the illuminated zone, called flame. The successive rarefication and compression of air during the propagation of sound wave also occur very fast. These processes approximate to and in the limiting sense may be called adiabatic

although they are not occurring in an isolated system. A process may be isothermal and at the same time adiabatic, e.g., the free expansion (expansion against zero pressure) of an ideal gas is associated with no heat change with the surroundings and no change in temperature.

If the change occurring in the system is such that after completion of the process the system returns to its initial state, the overall process is called a **cyclic process**.

3.2.6 Properties :

Classical Thermodynamics considers the behaviour of the macroscopic system and hence is concerned only with the macrosopic properties such as volume, pressure, temperature, surface tension, etc. without considering molecular model of matter and atomic properties such as distance between atoms in a crystal, i.e., statistical view point to the origin of such properties. The wide variety of macroscopic properties can be divided into two catagories—

Extensive and Intensive properties

(i) Extensive property -this property depends upon the mass of the system and is additive. Examples are mass, volume, surface area, force, kinetic energy, momentum, internal energy, entropy, Gibbs free energy, heat capacity, work, electrical energy etc.

(ii) Intensive property - this property is independent of mass and has the same magnitude throughout the homogeneous system when the system is under equilibrium condition otherwise it may vary from one portion to another portion. Examples are pressure, temperature, density, refractive index, boiling point, freezing point, viscocity coefficient, surface tension, molar heat capacity, molar internal energy, chemical potential etc. Moreover, the ratio of the two extensive properties. is an intensive property e.g.,

$$P = \frac{F}{A}; \quad \rho = \frac{M}{V}; \quad \eta = \frac{F}{A \times \frac{dv}{dz}} = \frac{\text{extensive}}{\text{extensive} \times \text{intensive}} = \text{intensive}$$

How can a property be characterised as intensive or extensive? To characterise the property as intensive or extensive at first determine the magnitude of the property for the whole system and then determine the magnitude of the same property for a portion of the system. If the magnitudes are found to be the same, the property is obviously an intensive property but if the magnitudes vary, the property is called an extensive property. e.g. water in a beaker boils at 100°C at 1 atm. If 10 gm of that water is taken in a test tube and is allowed to boil, it will also boil at 100°C under 1 atm. So b.pt. is an intensive property. On the other hand if the volume of water present in a beaker is 100 ml, then a portion of it will have lower volume. Total volume becomes the summation of the volumes of small portions of the systems taken. So volume is an extensive property.

Surface tension, viscosity, refractive index of a small portion of a solution have the same magnitude as those of the total solution. Hence they are intensive properties Colligative properties of a solution such as elevation of boiling point. depression of freezing point, osmotic pressure and relative lowering of vapour pressure are also intensive properties. Magnitude of such

3.7 Work :

The concept of work has emerged from our daily experience. In the macroscopic world if force acts on any system and exhibits its manifestation producing an observable effect in the surroundings, e.g., lifting or lowering of a mass, winding or unwinding of a spring, stretching of an wire etc — the effect produced by the action of the force is defined as work. From careful observation of innumerable effects happening in nature in the macroscopic world, men have gathered information regarding different types of forces operating in nature, e.g., when the leaves of a tree remain standstill we do not consider the presence of any unbalanced force i.e., directional movement of air. As soon as leaves start undulation, the concept of wind emerges out automatically. Such is the intimate relation between an unbalanced force and its effect. Here the movement of the leaves is the manifestation of work done by the wind. Similarly the act of free falling of the fruits brings the concept of another type of unbalanced force, i.e., gravitational force, into consideration. So long the leaves or the fruits remain attached to the tree we remain unaware about the manifestation of the gravitational force. The falling of mass is associated with work due to gravitational force.

Work can be classified as external work and internal work. External work has its manifestation in the surroundings. It includes expansion of a gas against an opposing force, rotation of wheel, bending of a rod, lifting of mass etc. External work is involved when point of application of force i.e., the boundary of the system shifts under the influence of the force. Internal work is the work, done by one portion of the system on the other portion having no observable effect produced in the surroundings. For example, the work done by molecules to overcome the intermolecular force of attraction is regarded as internal work. When a real gas expands against an opposing force by absorbing heat from the surroundings the external work considers the work associated with the observable change of the system, i.e., the volume change or the shifting of piston. During such volume expansion intermolecular separation also increases and molecules do work to move away from one another overcoming the intermolecular attractive force. This work is called the internal work and a portion of the supplied heat is utilised for this puprose. In thermodynamics by work we mean only the external work. If an ideal gas and a real gas expand against the same opposing force and undergo the same change in volume external work will be same in both the cases. In case of the real gas there will be internal work also.

Mechanical work, characterised by a change in volume of the system, has the magnitude equal to force multiplied by the displacement of the point of application of force. Thus, $|W| = F.\,ds$ where F = force and ds = External displacement. i.e., work is involved only when the force acting on the system has a non zero value and the displacement of the boundary is finite. In thermodynamics the term work is used in a more restricted manner than in mechanics. Here regarding work the following aspects must be considered.

(i) It is not a property of the system. Work is not present in the system before or after the change of the system. It is involved only during the change of state of the system through the displacement of boundary and is manifested at the boundary only.

(ii) Work must produce an effect in the surroundings.

(iii) (When the displacement occurs in the direction opposite to the applied force, the work is said to be done by the system on the surroundings and is given (–) ve sign and when the displacement occurs in the direction of the applied force work is said to be done on the system and is given (+) ve sign according to IUPAC convention In old convention work done by the gas is given (+) ve sign while work done on the gas is given (–) ve sign.)

(iv) When work is done on a system closed by adiabatic wall, the system receives work and the work becomes fully converted into energy of the system, which increases the chaotic, disordered motion i.e., thermal motion of the molecules and hence the temperature increases. Thus work may be considered as a mode of exchange of energy between system and surroundings involving ordered motion of the molecules during change of state of the system (Fig. 2).
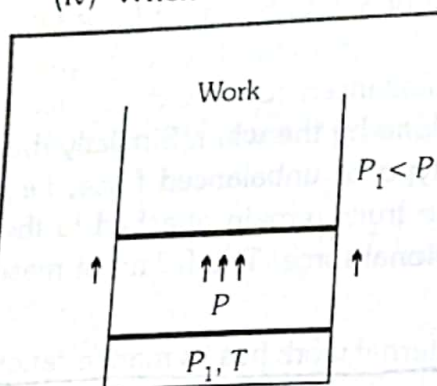

Fig. 2 Energy is transferred to the surroundings in the form of work due to ordered movement of molecules.

$P_1 < P$

P

P_1, T

Work

(v) Work is a path function and for the same change of state its magnitude depends upon the path of transformation of state of the system.

Work in general, of any type is the product of one intensive variable and the change in magnitude of an extensive variable caused under the influence of the intensive variable.

e.g., the mechanical work involved during the expansion of a gas under a pressure Popp is given by,

$$W = \text{Force} \times \text{displacement of the piston}$$
$$= -\text{Popp} \times \text{area of the piston} \times \text{displacement of the piston}$$
$$= -\text{Popp} \times \text{change in volume}$$
$$= -\text{Popp} . \Delta V.$$

Similarly other types of work involving different intensive variable are represented below.

The Nature of work	Expression of Work	Intensive variable	Extensive variable
Mechanical work	$-PdV$	P	V
Electrical work	$-EdZ$	E	Z
Extension of surface film	$-\gamma\, d\sigma$	γ	σ

3.8 Heat

(i) Like work, heat is also a mode of exchange of energy between system and the surroundings during the change of state of the system. It occurs through the boundary between the system and surroundings due to difference in temperature. Energy in the way of heat flows from higher to lower temperature. Heat is a form of energy in transit.

(ii) Like work, heat is not present in a system before or after the change of state of the system. What is present in the system is energy. Heat has its manifestation only in transit.

(iii) While work involves the exchange of energy through ordered, organised motion of the molecules, heat represents the dispersal of energy through disordered, chaotic movement of the molecules (Fig. 3).

(iv) The quantity of heat exchanged in a process is expressed in calorie and its magnitude represents the number of gms of water kept in the surroundings whose temperature changes by 1°C due to the exchange of that quantity of heat.

Fig. 3 Energy is transferred to the surroundings as heat due to chaotic movement of molecules

(v) The gaining of heat by a system is represented by a (+) ve sign while its release is represented by a (–) ve sign according to both IUPAC and old convention.
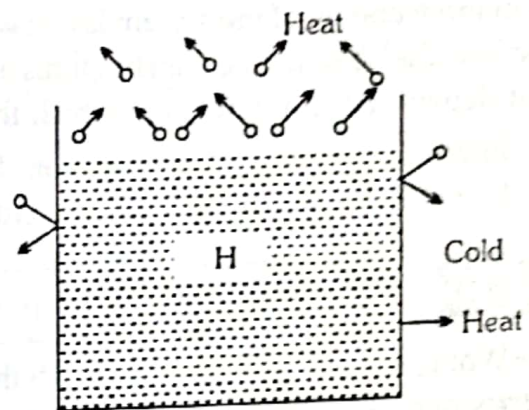
3.9 Internal Energy

Every system in this universe since its birth is a store house of energy and it is manifested only when either a change occurs in the system or a change is brought about by the system; e.g., it is difficult to convince one about the fact that a block of wood is a store house of energy until it is ignited to cause fire and heat or is allowed to fall on or thrown to any body to produce an effect, called work. As a whole the total energy (E) of a macroscopic system is given by the expression, $E = E_K + E_P + U$ where, E_K = Kinetic energy due to the movement of the system as a whole with respect to the external reference frame, E_P = Potential energy due to the presence of the system in external field of force. If the system is present in more than one type of field of forces (e.g., gravitational, electrical, magnetic etc) simultaneously, E_P represents the sum of different potential energy terms where each term is for one type of field of force.

U is the Internal energy of the system and is considered as the sum of—

(i) kinetic and potential energies of molecules associated with different internal modes of motion such as translation, rotation and vibration;

(ii) electronic energy;

emphasis on piston of different mass the piston is considered weightless and mass of the piston is considered together with the mass kept over the pistorn to exert the definite pressure. Hence to consider heat and work relationship for a give change in state of the system only frictionless, weightless piston is considered.

3.14 Ways of Transformation of State :

The two different ways by which the change of state of a system can be carried out, are best understood by considering the isothermal change of state of an ideal gas. For this purpose suppose one mole of an ideal gas is enclosed in a cylinder at temperature T, provided with a frictionless and weightless piston. The state is changed from (P_1, V_1) to (P_2, V_2) where $P_1 > P_2$.

(a) *Single step or finite step process :* The opposing pressure (P_1) is reduced to P_2 by reducing the mass kept over the piston in one step. As soon as the pressure is lowered the piston suddenly jumps upward and attains the final position. With this sudden change (i) a convection current of molecules is set up in the direction of the movement of the piston disturbing the mechanical equilibrium condition totally, (iii) fluctuation in temperature occurs destroying the thermal equlibrium condition and (iv) density at different portions fluctuates indicating the absence of material equilibruim condition. Thus during the single-step change of state, the system does not maintain the conditions of thermodynamic equilibrium. However, after the change has taken place the system gradually attains the new equilibrium state under the pressure P_2 and a definite period of time is required for this.

If the same change is carried out in finite number of steps instead of a single step, the character of the process in each step remains same as above — the only difference being that the system at each step attains equilibrium condition more rapidly than that of a single step process due to smallness in the difference of pressure between two successive steps. In this case, the change at each step is carried out only after the system has attained equilibrium condition in the previous step.

When the pressure is reduced from P_1 to P_2 in a single step, the gas expands against the pressure P_2 until its pressure becomes equal to P_2 (Fig. 4).

Here $|W_{expansion}| = P_{opp}(V_2 - V_1) = P_2(V_2 - V_1)$

$\qquad\qquad = $ Area EBCD.

To bring the gas to its initial state in a single step, the pressure is increased to P_1 and the gas is allowed to attain the volume V_1 under pressure P_1.

Work of compression, $= -P_1(V_1 - V_2) = $ Area AFCD (Fig.4).

Since $|W_{exp_1}| < W_{com_1}$ and ΔU in the two processes remains same in magnitude but opposite in sign, it. is
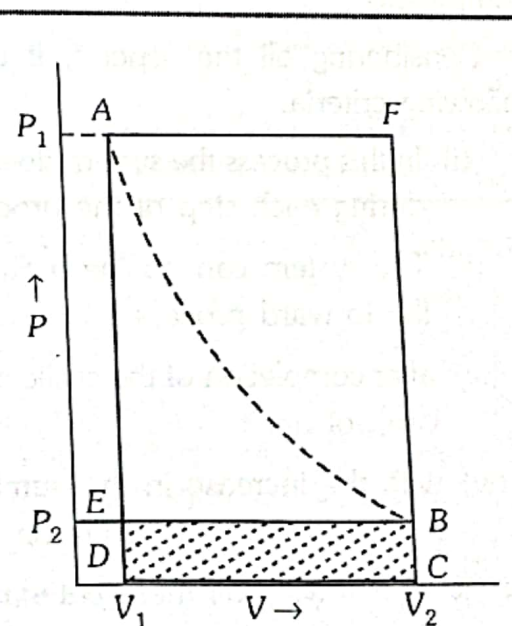

Fig. 4 W_{comp_1} is greater thatn $|W_{exp_1}|$

obvious that heat absorbed by the gas during expansion is less than the heat released by the gas, i.e., the forward and backward processes do not follow the same path.

If the expansion were carried out in two steps—in the first step, against a constant pressure P', and in the second step against the pressure P_2, the two-step expansion work is given by (Fig.5),
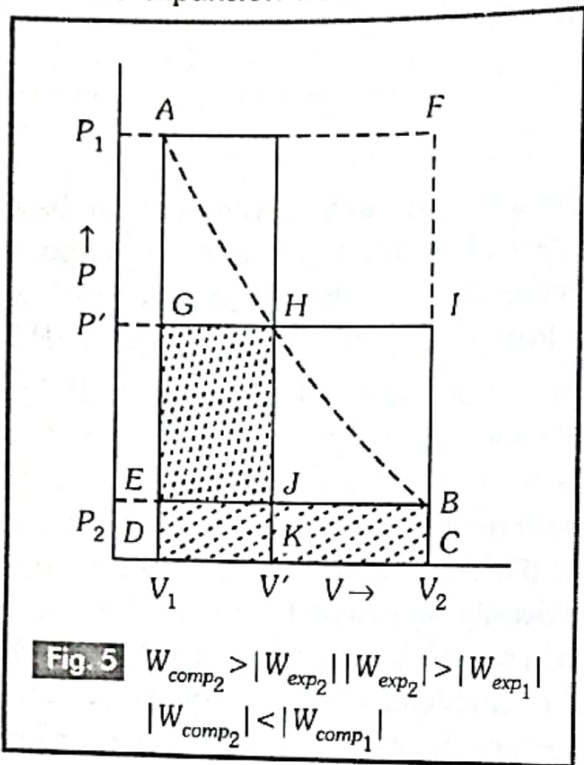
$$\left|W_{exp}\right| = P'(V'-V_1)+P_2(V_2-V')$$

$$= \text{Area GHKD + Area JBCK}$$

$$= \text{Area GHJBCD.}$$

Similarly, two step compression work is given by (Fig.5),

$$W_{comp2} = -\left[P'(V'-V_2)+P_1(V_1-V')\right]$$

$$= \text{Area HICK + Area ALKD}$$

$$= \text{Area ALHICD.}$$

Fig. 5 $W_{comp_2} > |W_{exp_2}| \, |W_{exp_2}| > |W_{exp_1}|$
$|W_{comp_2}| < |W_{comp_1}|$

In this case also $W_{comp2} > |W_{exp_2}|$ but the difference being less. This is true for any finite step process. Since in any finite step cyclic process $W_{comp} > |Wexp|$, heat absorbed during expansion is less than the heat released during compression. So, after the completion of the cycle the system returns to its initial state but the surroundings can not.

A two step process is better than one-step process in the sense that greater amount of work is obtained during two step expansion and lesser amount of work is to be done during the compression.

Considering all the aspects, it can be summarised that any finite step process has the following criteria.

(i) In this process the system does not maintain the conditions of thermodynamic equilibrium during each step of the process;

(ii) The system can not be brought to its initial state following the same path as that of the forward process,

(iii) after completion of the cyclic process the system returns to its initial state but surroundings can not and

(iv) with the increase in the number of steps work done by the system increases and the magnitude of work done on the system decreases.

Process following all these criteria is called an Irreversible process. Since in an irreversible process the system does not pass through equilibrium states all along, the irreversible path cannot be represented by solid line. It is rather represented by by broken line (- - -).

In a single step expansion where volume changes from V_i to V_f against opposing pressure P_{opp} the general expression for work is,

$$W_{exp_2} = - P_{opp} (V_f - V_i) \text{ where } P_f \geq P_{opp} \geq 0 \qquad \cdots \qquad \cdots \qquad (3.8)$$

When P_{opp} is less than P_f stoppers are to be provided in the cylinder so that gas does not expand beyond the volume V_f at pressure P_f. So in one step expansion the lower is the value of P_{opp} the lower will be $|W_{exp}|$ for the same volume change.

When $P_{opp} = 0$, $|W_{exp}| = 0$ and the expansion is called free expansion.

(b) Quasi-static change : The study of one-step and two step processes suggests that between the two given states with the increase in the number of steps, the work done by the system increases and similarly the work done on the system decreases.

When the expansion is carried out in large number of finite steps, the expansion at each step means the attainment of an intermediate equilibrium state. In each step the work obtained is represented by a narrow strip while in the corresponding step during compression the work done on the system is also represented by a similar narrow strip of same width but slightly larger area. So long the number of steps remains finite at any step during expansion the work obtained remains less than the work done in the corresponding step during compression (Fig.6).
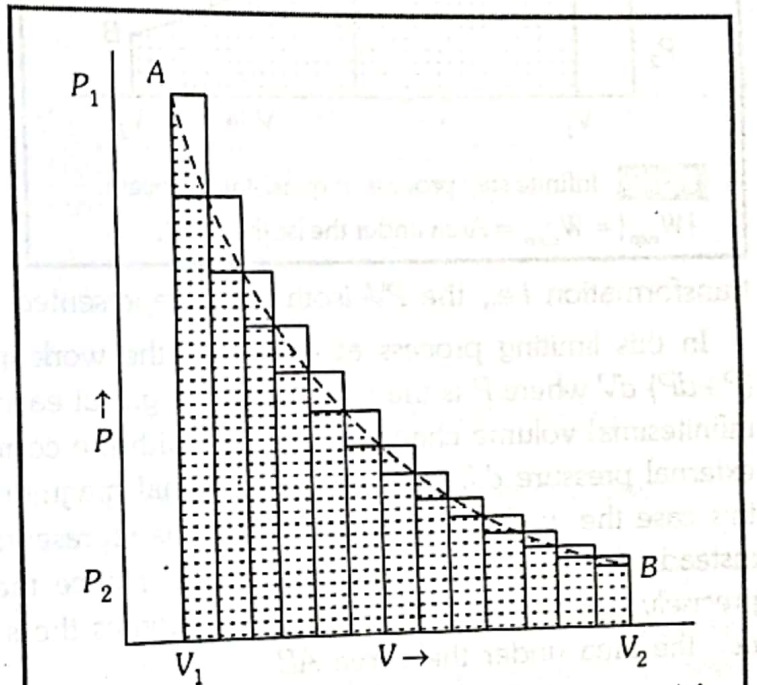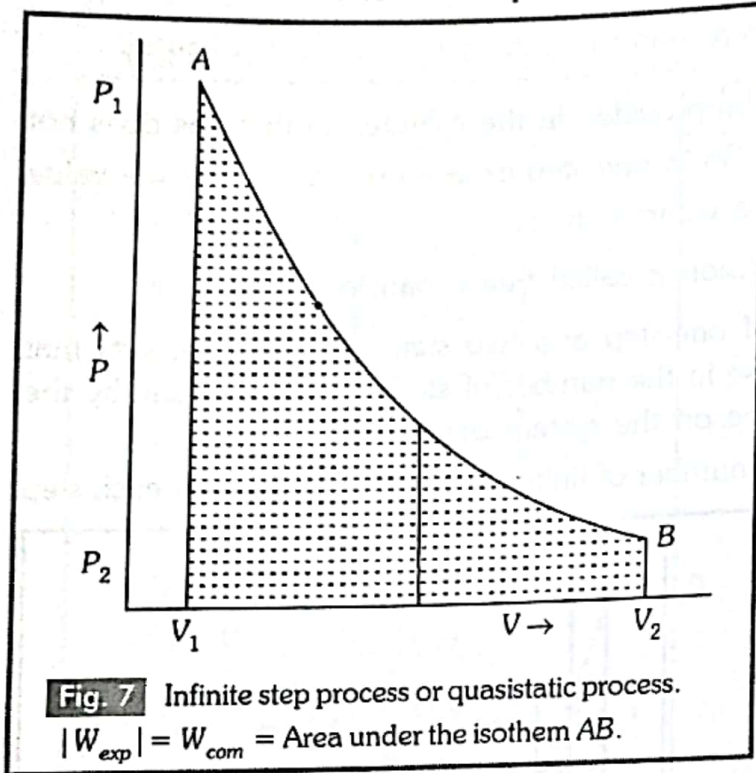
In a finite step process the total area under the lower stair case in the PV diagram represents the total work obtained during the expansion process and similarly the total area under the upper staircase represents the total work done during compression

Fig. 6 Finite step process. Area under the upper stair case $= W_{com}$ and area under lower stair case $= |W_{exp}|$

process. So, long the number of steps remains finite $W_{com} > |W_{exp}|$. However, with the increase in the number of steps difference between $|W_{exp}|$ and W_{com} decreases and in an infinite-step process the two areas become equal (Fig. 7), i.e., $|W_{exp}| = W_{comp}$.

Extending the concept of finite-step process if the expansion is carried out through infinite number of steps then the opposing pressure $(P - dP)$ at each step becomes infinitesimally less than the pressure (P) of the system by the magnitude dP. Here dP is as small as it could be so that if the opposing pressure just exceeds $(P - dP)$, virtually no change occurs. As dP is minimum, the difference between the two successive equilibrium states under pressures P and $(P - dP)$ is also minimum, i.e., the two equilibrium states are as close as possible. In any step as soon as the opposing pressure is made equal to $(P - dP)$ where P is the pressure of the

system, the system instantaneously passes from one equilibrium state to the adjacent another equilibrium state due to closest proximity. But however close may be the two states, a finite difference always exists between the two since dP is finite. Only in the limiting sense when dP tends to be zero, the differnece between the two states virtually disappears (Fig.7). Therefore, **in infinite step process the system undergoes a finite change in state i.e., from $(P_1 V_1)$ to (P_2, V_2) passing through adjacent intermediate equilibrium states virtually maintaining the equilibrium condition at each step of the process.** Such a process is called **quasi-static process.** Since a quasi-static process in the limiting sense passes through adjacent thermodynamic equilibrium states the points in the PV diagram representing successive equilibrium states in the limiting case touch one another and the path of transformation i.e., the PV isotherm is represented by a bold line.

Fig. 7 Infinite step process or quasistatic process. $|W_{exp}| = W_{com}$ = Area under the isothem AB.

In this limiting process at each step the work involved is given by either $(P-dP)dV$ or $(P+dP)dV$ where P is the pressure of the gas at each step before the change and dV represents infinitesimal volume change associated with the corresponding change of the system when the external pressure differs by an infinitesimal magnitude of dP from the pressure of the gas. In this case the work involved in any step is represented by a vertical line of infinetisimal width instead of a narrow strip of finite width. Hence the work involved at each step can not be precisely determined. The total work becomes the summation of area of all the vertical lines, i.e., the area under the curve AB.

So, $W_{exp} = -[(P_1 - dP)dV + (P' - dP)dV + (P'' - dP)dV + ... + P_2 dV]$

where $P' = P_1 - dP$ and $P'' = P' - dP$ etc.

Neglecting $dPdV$ from each term,

$$W_{exp} = [P_1 dV + P'dV + P''dV + ... P_2 dV]$$

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

$$= -\text{Area under the } PV \text{ curve}$$

$$\therefore \ |W_{exp}| = \text{Area under the isotherm } AB \text{ (Fig.7)}$$

For n mole of an ideal gas during isothermal quasi-static expansion

$$W_{exp} = -\int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln\frac{V_2}{V_1}$$

$$\therefore |W_{exp}| = nRT \ln\frac{V_2}{V_1} \qquad \qquad \cdots \qquad \cdots \qquad (3.9)$$

[In old convension $W_{exp} = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln\frac{V_2}{V_1}$]

For a given volume change, as in each step opposing pressure $(P - dP)$ is as maximum as it could be, in quasi-static process $|W_{exp}|$ becomes maximum.

In quasi-static compression process involving infinite step, the limiting work of compression is,

$$W_{com} = -[(P_2 + dP)dV + \ldots\ldots\ldots + (P_1 - dP + dP)dV]$$

$$= [P_2 dV + \ldots\ldots\ldots\ldots + P_1 dV] \text{ as } dPdV \text{ is negligibly small.}$$

$$= -\int_{V_2}^{V_1} PdV = \int_{V_1}^{V_2} PdV = \text{Area under the PV isotherm AB (Fig.7).}$$

For n mole of an ideal gas undergoing isothermal quasi-static compression.

$$W_{comp} = -\int_{V_2}^{V_1} \frac{nRT}{V} dV = nRT \ln\frac{V_2}{V_1} \qquad \qquad \cdots \qquad \cdots \qquad (3.10)$$

[In old convention, $W_{comp} = -\int_{V_2}^{V_1} \frac{nRT}{V} dV = nRT \ln\frac{V_2}{V_1} \quad \therefore |W_{comp}| = nRT \ln\frac{V_2}{V_1}$]

For a given decrease in volume at each step of quasi-static compression as the opposing pressure $(P - dP)$ is as minimum as it could be it can be stated that W_{com} is minimum at each step during quasi-static compression. So W_{com} is minimum in a quasi-static process.

The basic difference between the two processes lies in the fact that in an irreversible process the driving force in each step is of appreciable magnitude whereas in quasi-static process involving infinitely large number steps, the driving force at each step is infinitesimally as small as it could be and in the limiting sense it virtually disappears. Quasi-static process is an extremely slow process.

To understand a quasi-static process suppose a liquid in equilibrium with its vapour is enclosed in a cylinder at temperature and under a pressure P which is the vapour pressure of the liquid at the given temperature. The equilibrium condition exists between liquid and vapour so long the state parameters remain unchanged. If the pressure is slightly lowered by dP, i.e., the opposing pressure becomes $(P - dP)$ the following subsequent changes then occur —

(i) The vapour initially present at P undergoes sudden expansion to attain the pressure $(P - dP)$, however small be dP.

(ii) As soon as the vapour pressure decreases from $(P - dP)$, the equilibrium condition between liquid and vapour is infinitesimally disturbed.

Phy Chem-22