

[THERODYNAMICS]

[B.Sc – I]

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[01/08/2021]

THERMODYNAMICS

Introduction:- The word 'Thermodynamics' implies flow of heat. The subject however, is much more comprehensive or general. It deals with energy changes accompanying all types of physical and chemical processes.

Thermodynamics is based on three simple laws. These laws are not derived. These are generalization deduced from are long experience with energy.

Importance of Thermodynamics:-

- (1) Most of the important generalizations of physical chemistry, including Van't Hoff law of dilute solution, Raoult's law of vapor pressure lowering, distribution law, law of chemical equilibrium, the phase rule and the laws of thermochemistry can be deduced from the laws of thermodynamics.
- (2) Thermodynamics helps to predict whether a given process or a chemical, reactions of temperature, pressure and concentration. It also helps us to determine the extent to which a process, including a chemical reaction can proceed.

Limitation of Thermodynamics:-

- (1) The laws of thermodynamics apply the behaviour of assemblages of a vast – member of molecules and not to individual molecules.
- (2) Thermodynamics can only predict whether a given process, including a chemical reaction is feasible or not,

but it does not tell anything about the rate at which a given process may proceed.

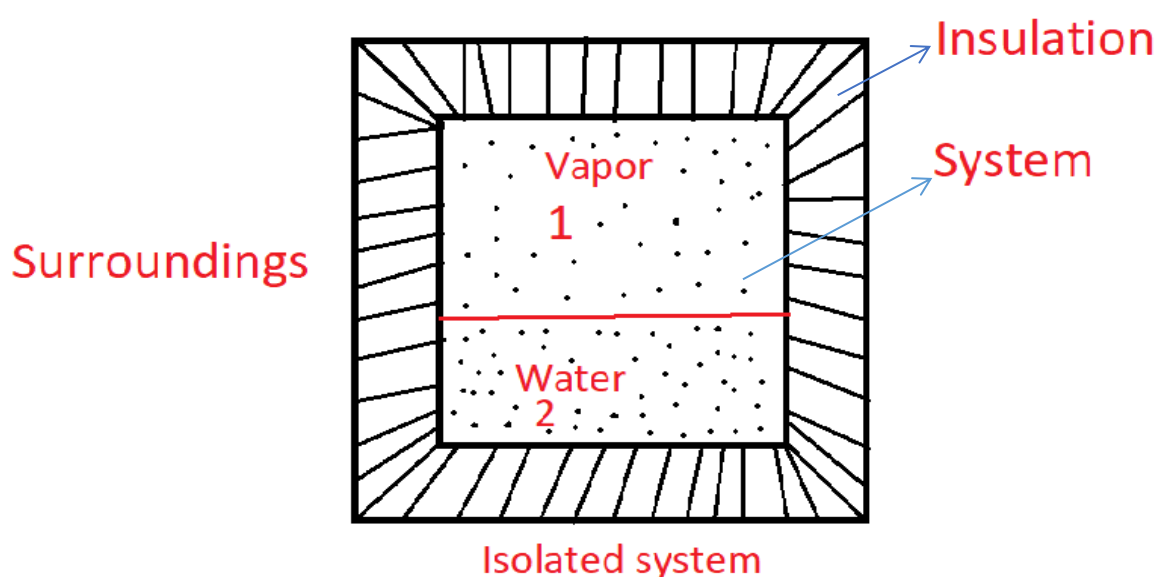
Terminology of Thermodynamics:-

System:- A system may be defined as any specified portion of matter under study which is separated from the rest of the universe with a bounding surface.

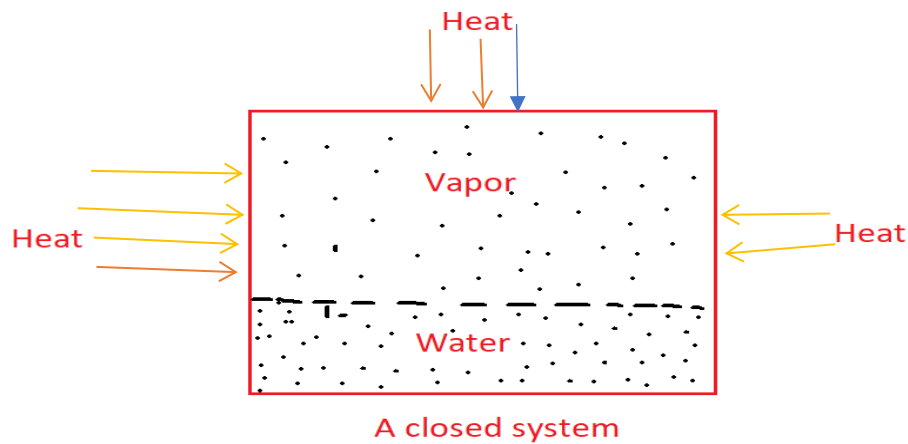
Surroundings:- The rest of the universe which might be in a position to exchange energy and matter with the system is called the surroundings.

There are three types of system.

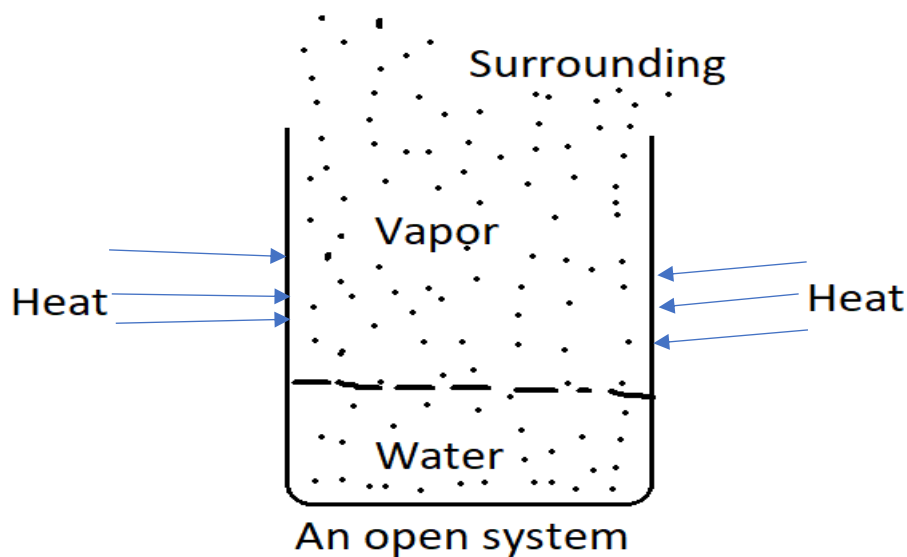
- (i) Isolated system.
 - (ii) Closed system.
 - (iii) Open system.
- (1) **Isolated system:-** A system which can exchange neither energy or matter with its surrounding is called an isolated system.



- (2) **Closed system:-** A system which can exchange energy but not matter with its surroundings is called closed system.



- (3) **Open system:-** A system which can exchange matter as well as energy with its surroundings is said to be an open system.



Phase:- A phase is defined as a homogeneous and physically distinct part of a system which is bounded by a surface and is chemically separable from other parts of the system.

Homogeneous system:-

A system is said to be homogeneous. When it is completely uniform throughout.

Ex:- A pure solid, a liquid, a solution, mixture of gases.

In other, words a homogeneous system consist, of only one phase.

Heterogeneous system:- A system is said to be heterogeneous when it is not uniform through.

Examples:-

- (i) Two or more immiscible liquids.
- (ii) A solid is contact with a liquid in which it does not dissolve.
- (iii) A liquid is contact with its vapor.

Thermodynamics equilibrium:-

A system in which the macroscopic properties do not undergo any change with time is said to be in thermodynamically equilibrium.

Suppose a system is heterogeneous I,e it consist of more than one phase. Then, if it is equilibrium the macroscopic properties in the various phase remain unaltered with time.

Actually, the term thermodynamics equilibrium implies the existence of three kinds of equilibria in the system. These are-

- (i) **Thermal equilibrium:-** A system is said to be in thermal equilibrium if there is no flow of heat from one portion

of the system to another. This is possible if the temperature remains the same throughout all parts of the system.

(ii) **Mechanical equilibrium:-** A system is said to be in mechanical equilibrium if no mechanical work is done by one part of the system on another part of the system. This is possible if the pressure, remain the same through all parts of the system.

(iii) **Chemical equilibrium:-** A system is said to be in a chemical equilibrium if the composition of the various phase in the system remains the same throughout.

Extensive property:- An extensive property of a system is that which depends upon the amount of the substance or substance present in the system. The examples are mass, volume, energy and surface area.

Intensive property:- An intensive property of a system is that which is independent of the amount of the substance present in the system. The examples, are temperature, pressure, density, viscosity, refractive index, surface tension, specific heat etc. M.P, B.P.

Process:- Whenever a system changes from one state to another, it is accompanied by change in energy. In the case of open systems, there may be change of matter as well.

Diff:- By a process, we mean the path or the operation by which a system changes from one state to another.

On the basis of condition four different types of processes

are known-

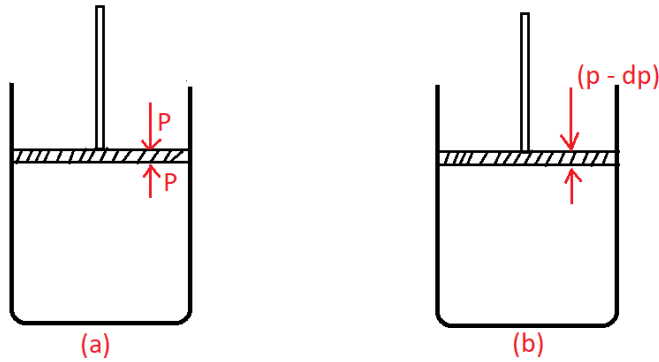
- (1) **Isothermal process:-** A process is said to be isothermal if the temperature of the system remains constant during each step of the process.
- (2) **Adiabatic process:-** A process is said to be adiabatic if no heat enters or leaves the system during any step of the process.
- (3) **Isobaric process:-** A process is said to be isobaric if the pressure of the system remains constant during each step of the change in the state of the system.
- (4) **Isochoric process:-** A process is said to be isochoric if the volume of the system remains constant during each step of the process.

Reversible and Irreversible process:-

On the basis of nature processes are of two types.

Reversible and Irreversible:- The change of a system from one state to another may occur either in a reversible or in an irreversible way.

Reversible process:- In a reversible process, the change of the system is allowed to happen slowly in mixture quantities (infinitesimally slowly) until the whole of the specified change is achieved.



Characteristic:-

- (i) In an ideally reversible process, the change must occur in successive stages of infinitesimal small quantities.
- (ii) The small changes should be carried out in such a way that, throughout the transition, the system must be maintaining virtual thermodynamics equilibrium, at each of the small stages.

A process is said to be thermodynamically reversible, if the amount of heat energy changed is the same in both forward process and backward process.

A truly reversible process, has to be carried out in infinitesimal amounts and hence would require infinite time.

In practice, the small changes in a process have definite magnitudes and are thus only close approximations at the best to a true reversible process. A strictly reversible process is thus purely a concept; nevertheless, it is extremely useful in the analysis of our problems of energy changes.

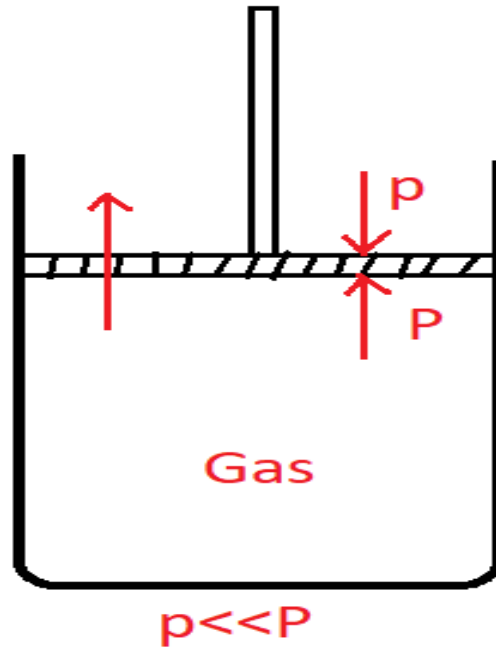
Irreversible process Diff:- An irreversible process is one which occurs suddenly or spontaneously without the

restriction of occur in successive stages of infinitesimal quantities.

Characteristic:-

- (i) The system would also not remain in virtual equilibrium during the transition.
- (ii) The system after undergoing a change will have the tendency to return to the initial state by itself. If the change be reversible and the system is made to go back to the initial state, the work (w) is the forward direction and in the backward process would be unequal. It is important to remember that if the initial and final stages be specified, the internal energy change would always be the same. Whether the process has been, effected reversibly or irreversibly. In an irreversible process, since work terms (dw) in the two opposite, direction are unequal, the heat transfers (dq) would also be unequal.

If the amount of heat changed in forward process is different from the amount of heat changed in the reversible process, then the process is said to be irreversible process.

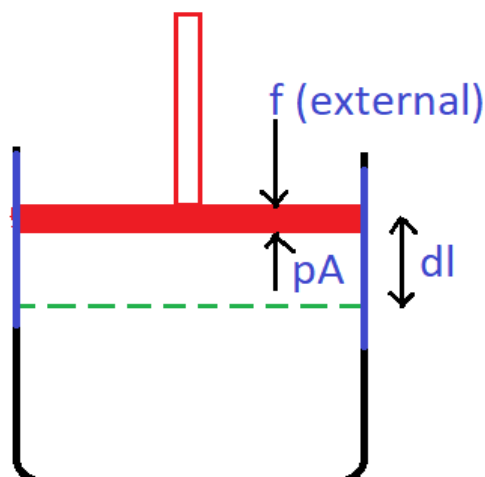


Difference between Reversible and Irreversible process:-

Reversible process	Irreversible process
(i). It is an ideal process.	(i). It is natural process. All most all natural, process are irreversible.
(ii). It is infinitesimally slowly process.	(ii). It is a rapid process.
(iii). The work is maximum.	(iii). The work is less than reversible process.
(iv). It requires infinite time.	(iv). It require very small time.
(v). Example:- (a). Reaction of electrolytic cell. (b). All isothermal and adiabatic process occurring very slowly.	(v). All natural process:- (a). Flow of heat from higher to lower temperature. (b). Flow of water from higher to lower level. (c). Diffusion of gas.

Mechanical work:-

Mechanical work is done whenever there is a change (increase or decrease) in the volume of a system.



Let us consider a gas in closed in a cylinder provided with a piston. If P is the pressure of the gas, it exerts a force f on the piston given by

$$F = PA, (\because P = \frac{F}{A})$$

Where A is the area of cross – section of the piston. This force can be balanced by an equal force, F (external) acting on the piston, as shown in the figure. If there is an infinitesimally small amount of expansion of the gas resulting from an infinitesimally small movement of the piston (dl) ‘ontward’ the small amount of work done (dw) by the gas (system) on the surroundings will be given by

$$\begin{aligned} dE \text{ or } dw &= F_{\text{ext}} \times dl \text{ (work = Force x displacement)} \\ &= P \times A \times dl \end{aligned}$$

Or, $dw = \frac{F_{ext}}{A} \times A \times dl$

$$dw = P \times dv$$

$$dw = p dv$$

Here, force is external (F_{ext}) because it external to the system and the distance through which this force act.

Where, dv is the small increases in volume of the gas that has taken place in that process. This process of expansion may be carried out infinitesimally slowly (i.e. in a thermodynamically reversible manner) in a series of steps.

The work done in each step will be given by Pdv . If ultimately, the volume of the system changes by a finite quantity, say from V_1 to V_2 , then the total work (w) done by the system on the surroundings will be obtained by the integration of the factor Pdv i.e.

$$w = \int_{V_1}^{V_2} P dv$$

If, on the other hand, there is infinitesimal contraction of the gas resulting from infinitesimal movement of the piston inward, then the small amount of work done by the surrounding on the system will be given by

$$dw = PdV$$

where dv is the small decrease in volume of the gas that has taken place in the process. If the work of concentration is carried out in the above manner in a series of steps, the work

done (w) **by the surroundings on the system** is given by the integration of the factor PdV .

$$w = \int_{V_1}^{V_2} Pdv$$

When the volume of the system decreases from V_1 to V_2 .

Mechanical work at constant pressure:-

If the pressure P remains constant throughout the process the above integration gives.

$$\begin{aligned} W &= P (V_2 - V_1) \\ &= P\Delta V \end{aligned}$$

Because, the integration of constant p is also P .

In the case of expansion of a gas, the work is done by the system on the surroundings and w has a positive value.

In the case of contraction of a gas the work is done by the surroundings on the system and w has a negative value.

Some mathematical terms:-

Let us suppose a function X depends on y and z .

i, e $X = f(y, z)$

Change in X may be written by the following three methods-

- (i) Very small change in $X = dx$
- (ii) Large change in $x = \Delta x$
- (iii) Partial change in $x = \delta x$

Now,

$$dx = \left(\frac{\delta x}{\delta y} \right)_z dy + \left(\frac{\delta x}{\delta z} \right)_y dz$$

Example:-

$$(i) \quad E = f(V, T)$$

$$\therefore dE = \left(\frac{\delta E}{\delta V}\right)_T \delta V + \left(\frac{\delta E}{\delta T}\right)_V \delta T.$$

$$(ii) \quad H = f(T, P)$$

$$\therefore dH = \left(\frac{\delta H}{\delta T}\right)_P \delta T + \left(\frac{\delta H}{\delta P}\right)_T \delta P.$$

$$(iii) \quad G = f(T, P, N)$$

$$\therefore dG = \left(\frac{\delta G}{\delta T}\right)_{P,N} \delta T + \left(\frac{\delta G}{\delta P}\right)_{T,N} \delta P + \left(\frac{\delta G}{\delta N}\right)_{T,P} \delta N.$$

Maximum work:-

According to the equation of work done.

$$W = \quad = P\Delta V$$

Now, let us suppose the pressure applied on the piston is negligibly small in comparison with the pressure of the gas inside the cylinder. The gas will expand rapidly, i.e. irreversibly. In this case the work done by the system will be negligibly small since the opposing force has been negligibly small. If the opposing force on the piston is zero, the work done by the system will be zero, i.e.

$$P_{(\text{external})} \times \Delta V = 0$$

Hence, it follows that when a gas expands freely, i.e. when it expands against vacuum such that $P_{(\text{external})} = 0$ no work is done by the system.

It also follows from the above discussion that the magnitude of work done by a system on expansion depends upon the magnitude of the opposing (external)

pressure. The closer is the opposing pressure to the pressure of the gaseous system in the cylinder, the greater will be the work performed by it on expansion. In other words, maximum work is obtained when the two opposing pressures differ only by infinitesimally.

Small amount from one another ideal reversible process. This condition is demanded for an reversible process. Hence, maximum work is done for thermodynamic.

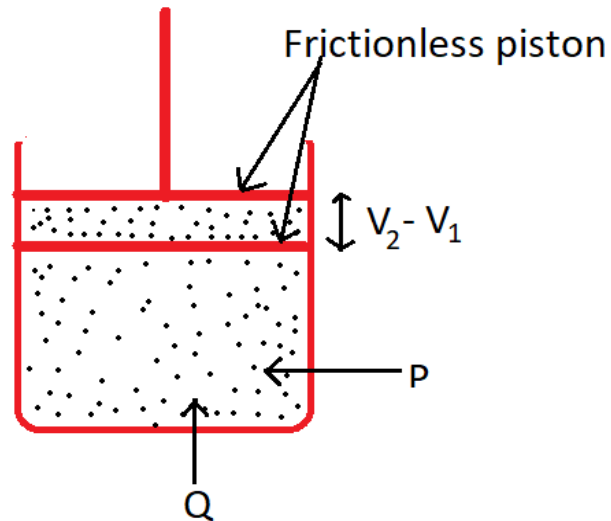
" The first law of thermodynamics"

"According to this law the energy of a system is conserved in other words energy can neither be created nor be destroyed, however one form of energy" can be converted in to another form.

This law is also called as "law of conservation of energy".

The law is based an experience of ages that it is impossible to constant a perpetual machine (it is a machine which can produce energy without expenditure of energy).

Mathematical formulation of First law of Thermodynamics:-



Let us suppose a gas is closed in a vessel with a frictionless piston.

Again,

Pressure of the gas = P

Energy of the gas = E_1

Volume of the gas = V_1

Now, let us suppose Q amount of heat is supplied from outside. As a result of this following two changes will take place.

- (i) Energy of the gas will increase suppose final energy becomes E_2

Thus,

Change in energy = $\Delta E = (E_2 - E_1)$

- (ii) Expansion of gas will occur against the pressure P on piston and work will be done.

Suppose work done due to expansion is " w " and final volume of gas is " V_2 ".

Then, change in volume $\Delta V = (V_2 - V_1)$

So, $W = \text{pressure} \times \text{change in volume}$

$$W = P\Delta V$$

Now, according to first law of thermodynamics-

$$Q = \Delta E + P\Delta V \longrightarrow \text{(i)}$$

Now, for small change,

$$q = dE + P\Delta V \longrightarrow \text{(ii)}$$

$$\text{or, } q = dE + W \longrightarrow \text{(iii)}$$

$$\text{or, } dE = q - W \longrightarrow \text{(iv)}$$

Equation i, ii, iii, and iv represent first law of thermodynamics.

According to Einstein's theory of relatively mass can also be converted in to energy and the relationship is $E = mc^2$.

Hence,

$E = \text{energy}$

$m = \text{mass lost}$

$C = \text{velocity of light}$

In all energy transformation, q is given a positive sign when heat is absorbed and a negative sign when work heat is evolved by the system. Work, w is positive when work is done by the system and negative when work is done on the system.

So, in the light of this theory we can have modified statement of first law of thermodynamics as.

"The energy and mass both of a system is conserved".

Application:- This law gives a very importance thermodynamic function, enthalpy or heat content (H).

Heat content or Enthalpy:-

Let us suppose that the change of state of a system is brought about at constant pressure. In such case there will be change of volume, if q amount of heat is supplied. Let the volume increases from V_1 to V_2 at constant pressure P .

Then the work done (w) by the system will be,

$$W = P (V_2 - V_1) \longrightarrow (1)$$

Now, from First law of thermodynamics

$$q = \Delta E + W$$

or, $\Delta E = q - W \longrightarrow (2)$

Putting the value of W from equation (1) to equation (2) we have-

$$\Delta E = q - P (V_2 + V_1)$$

Or, $E_2 - E_1 = q - P (V_2 + V_1)$

Or, $E_2 - E_1 = q - PV_2 + PV_1$

Or, $E_2 + PV_2 - E_1 - PV_1 = q$

Or, $(E_2 + PV_2) - (E_1 + PV_1) = q \longrightarrow (3)$

Here, $(E_2 + PV_2)$ and $(E_1 + PV_1)$ are called as enthalpies.

In general enthalpy, H can be represented as,

$$H = E + PV$$

Thus, Enthalpy can be defined as-

“The total energy stored in a system is called as enthalpy or heat content of a system”.

Since, E is a definite quantity and P and V are also definite properties which define state of the system, H is also a definite property depending upon state of the system.

Now, from equation (3) we have-

$$H_2 - H_1 = q$$

$$\text{Or, } \Delta H = q \longrightarrow (4)$$

Again, putting the value of q from equation (4) to equation (3) we have-

$$(E_2 + PV_2) - (E_1 + PV_1) = \Delta H$$

$$\text{Or, } E_2 + PV_2 - E_1 - PV_1 = \Delta H$$

$$\text{Or, } E_2 - E_1 + PV_2 - PV_1 = \Delta H$$

$$\text{Or, } (E_2 - E_1) + P(V_2 - V_1) = \Delta H$$

$$\text{Or, } \Delta E + P\Delta V = \Delta H$$

$$\text{Or, } \Delta H = \Delta E + P\Delta V$$

Characteristics of Enthalpy:-

- (i) H is a state function and depends only on the state of the system and not on the path.
- (ii) H is a thermodynamics function.
- (iii) H is a extensive property.

Heat capacity:-

“The amount of heat required to raise the temperature of a system by 1°C is called as heat capacity”. It is an extensive property.

Specific heat capacity:-

“The amount of heat required to raise the temperature of one gram of a system by one, degree centigrade is called specific heat capacity of the system”. Heat capacity is denoted by C .

Suppose 'q' amount of heat is required to raise the temperature by ΔT . Then heat capacity C,

$$C = \frac{q}{\Delta T}$$

For small change,

$$C = \frac{dq}{dT}$$

For gases, there are two types of heat capacity-

(1) Heat capacity at constant pressure (Cp):-

"The amount of heat required to raise the temperature of a gas by 1^oc at constant pressure is called as Cp".

Since, at constant pressure, heat supplied is q_p and temperature raised is ΔT

Then,

$$C_p = \frac{q_p}{\Delta T} \longrightarrow (1)$$

(2) Heat capacity at constant volume (Cv):-

"The amount of heat required to raise the temperature of a gas by 1^oc at constant volume is called as Cv".

Suppose 'q_v' amount of heat is needed to raise the temperature by ΔT ,

$$C_v = \frac{q_v}{\Delta T} \longrightarrow (2)$$

Thermodynamic definition of Cp and Cv :-

Cp By definition,

$$C_p = \frac{q_p}{\Delta T} \longrightarrow (1)$$

Here, q_p = Heat given at constant P

ΔT = Change in temperature

Now, from the first law of thermodynamics, we know that

$$q_p = \Delta T + P\Delta V \longrightarrow (2)$$

and, $H = E + PV$

$$\therefore \Delta H = \Delta E + P\Delta V \longrightarrow (3)$$

At constant P

On combining equation (2) and (3) we get,

$$q_p = \Delta H \longrightarrow (4)$$

On putting the value of q_p from equation (4) in equation (1) we get,

$$C_p = \frac{\Delta H}{\Delta T} \longrightarrow (5)$$

For small change,

$$C_p = \frac{dH}{dT} \longrightarrow (6)$$

For particle change,

$$C_p = \left(\frac{\delta H}{\delta T}\right)_P \longrightarrow (7)$$

Equation (5), (6) and (7) are the thermodynamics definition of C_p .

C_v By definition,

$$C_v = \frac{q_v}{\Delta T} \longrightarrow (1)$$

Where, q_v = Heat given at constant volume

ΔT = Change in temperature

From the first law of thermodynamics,

$$q = \Delta E + P\Delta V$$

At constant volume, $\Delta V = 0$

$$\therefore q_v = \Delta E$$

On putting the value of q_v from equation (2) to equation (1), we have,

$$C_v = \frac{\Delta E}{\Delta T} \longrightarrow (3)$$

From small change,

$$C_v = \frac{dE}{dT} \longrightarrow (4)$$

For partial change,

$$C_v = \frac{\delta E}{\delta T} \longrightarrow (5)$$

Equation (3), (4) and (5) are thermodynamics definition of C_v .

Relation between C_p and C_v

For

Prove that for an ideal gas $C_p - C_v = R$

Ans:- By thermodynamic definition of C_p and C_v , we know that,

$$C_p = \frac{dH}{dT} \longrightarrow (i)$$

$$C_v = \frac{dE}{dT} \longrightarrow (ii)$$

Since, $H = E + PV$

So, $dH = dE + PdV$

By dividing dT on both sides, we get,

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{PdV}{dT} \longrightarrow (iii)$$

On putting the value from (i) and (ii) to equation (iii) we get,

$$C_p = C_v + \frac{PdV}{dT} \longrightarrow (4)$$

Now, for one mole of an ideal gas

$$PV = RT$$

$$\therefore PdV = RdT$$

$$\text{Or, } R = \frac{PdV}{dT} \longrightarrow (5)$$

On putting the value from equation (5) to equation (4) we have,

$$C_p = C_v + R$$

$$\text{Or, } C_p - C_v = R$$

This prove that relationship.

Molar Heat capacity:-

“The amount of heat required to raise the temperature of one mole of the substance by 1°k or 1°c is called as molar heat capacity of the substance”.

$$C_m = \frac{q_m}{\Delta T}$$

Isothermal Reversible work done:-

Let us suppose an ideal gas absorbs ‘q’ amount of heat and is expanded from V_1 to V_2 at constant temperature T.

Now, from the first law of thermodynamics-

$$q = \Delta T + P\Delta V \longrightarrow (1)$$

Since, temperature is constant and

$$\text{So, } \Delta T = 0$$

Thus, equation (1) becomes,

$$q = \Delta T + P\Delta V \longrightarrow X$$

$$\text{or, } q = P\Delta V = W_{\text{iso}}$$

$$\text{or, } q = W_{\text{iso}} = P\Delta V$$

On integration, we get

$$q = W_{\text{iso}} = \int_{V_1}^{V_2} PdV \longrightarrow (2)$$

For n mole of an ideal gas, we know that

$$PV = nRT$$

$$\therefore P = \frac{nRT}{V} \longrightarrow (3)$$

On putting the value of P from (3) in (2), we get,

$$q = W_{\text{iso}} = \int_{v_1}^{v_2} nRT \frac{dV}{V}$$

$$= nRT \int_{v_1}^{v_2} \frac{dV}{V}$$

$$q = W_{\text{iso}} = nRT_{v_1} [\ln V]^{v_2}$$

$$q = W_{\text{iso}} = nRT [\ln V_2 - \ln V_1]$$

$$W_{\text{iso}} = nRT \ln \frac{v_2}{v_1}$$

$$q = W_{\text{iso}} = 2.303 nRT \ln \frac{v_2}{v_1} \longrightarrow (4)$$

Since, at constant temperature,

$$P_1 V_1 = P_2 V_2$$

$$\therefore \frac{v_2}{v_1} = \frac{P_1}{P_2}$$

So, equation (4) may become-

$$q = W_{\text{iso}} = 2.303 nRT \log_{10} \frac{v_2}{v_1} \longrightarrow (5)$$

Equation (4) and (5) are expression for isothermal work done.

Adiabatic work done:-

From the first law of thermodynamics-

$$q = dE + w$$

For adiabatic process,

$$q = 0$$

$$\therefore 0 = dE + W_{\text{adia}} \longrightarrow (1)$$

$$\therefore W_{\text{adia}} = -dE$$

\therefore By definition of C_v , we know that,

$$C_v = \frac{dE}{dT}$$

$$\therefore dE = C_v \cdot dT \longrightarrow (2)$$

On putting the value of dE from (2) to (1), we get-

$$dE = -C_v \cdot dT$$

On integration, we get

$$\begin{aligned} W_{\text{adia}} &= -\int_{T_1}^{T_2} C_v \cdot dT = -C_v \int_{T_1}^{T_2} dT \\ &= -C_v [T]_{T_1}^{T_2} = -C_v [T_2 - T_1] \end{aligned}$$

$$\text{Or, } W_{\text{adia}} = -C_v [T_2 - T_1] \longrightarrow (3)$$

This is the expression of adiabatic work done.

➤ Prove that for adiabatic process $PV^\gamma = \text{constant}$:-

Ans:- From first law of thermodynamics,

$$q = dE + PdV$$

For adiabatic process,

$$q = 0$$

Then,

$$0 = dE + PdV$$

$$\text{Or, } dE = -PdV \longrightarrow (1)$$

Now,

$$\therefore C_v = \frac{dE}{dT} \text{ at constant } V$$

$$\text{Or, } C_v \cdot dT = dE \longrightarrow (2)$$

Putting the value of dE from equation (2) to (1), we have,

$$C_v \cdot dT = - PdV \longrightarrow (3)$$

For an ideal gas for one mole,

$$PV = RT$$

$$\therefore P = \frac{RT}{V} \longrightarrow (4)$$

Putting the value of P from equation (4) to equation (3) we get,

$$C_v \cdot dT = - RT \cdot \frac{dV}{V} \longrightarrow (5)$$

On integration we get,

$$\int_{T_1}^{T_2} C_v \frac{RT}{V} = - \int_{v_1}^{v_2} R \frac{dV}{V}$$

$$\text{Or, } C_v [\ln T]_{T_1}^{T_2} = - R [\ln V]_{V_1}^{V_2}$$

$$\text{Or, } C_v \ln \frac{T_2}{T_1} = - \ln \frac{v_2}{v_1}$$

$$\text{Or, } C_v \ln \frac{T_2}{T_1} = R \ln \frac{v_1}{v_2} \longrightarrow (6)$$

Now,

$$\text{Since } C_p - C_v = R \longrightarrow (7)$$

Putting the value of R from equation (7) to equation (6) we have,

$$C_v \ln \frac{T_2}{T_1} = (C_p - C_v) \ln \frac{v_1}{v_2}$$

$$\text{Or, } \ln \frac{T_2}{T_1} = \frac{C_p - C_v}{C_v} \ln \frac{v_1}{v_2}$$

$$\text{Or, } \ln \frac{T_2}{T_1} = \left[\frac{C_p}{C_v} - 1 \right] \ln \frac{v_1}{v_2}$$

$$\therefore \frac{C_p}{C_v} = \gamma$$

$$\therefore \ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{v_1}{v_2}$$

$$\text{Or, } \ln \frac{T_2}{T_1} = \ln \left[\frac{v_1}{v_2} \right]^{\gamma - 1}$$

$$\text{Or, } \frac{T_2}{T_1} = \left[\frac{v_1}{v_2} \right]^{\gamma - 1} \longrightarrow (8)$$

Now,

$$\text{For ideal gas, } \frac{P_1 v_1}{T_1} = \frac{P_2 v_2}{T_2}$$

$$\text{Or, } \frac{T_2}{T_1} = \frac{P_2 v_2}{P_1 T_1} \longrightarrow (9)$$

On putting the value of T_2/T_1 from equation (9) to equation (8) we get,

$$\frac{P_2 v_2}{P_1 T_1} = \left[\frac{v_1}{v_2} \right]^{\gamma - 1}$$

$$\text{Or, } \frac{P_2}{P_1} = \left[\frac{v_1}{v_2} \right]^{\gamma - 1} \left[\frac{v_1}{v_2} \right]^1 = \left[\frac{v_1}{v_2} \right]^{\gamma - \gamma + \gamma}$$

$$\text{Or, } \frac{P_2}{P_1} = \left[\frac{v_1}{v_2} \right]^{\gamma}$$

$$\text{Or, } P_1 v_1^{\gamma} = P_2 v_2^{\gamma}$$

$$\text{Or, } P v^{\gamma} = \text{constant.}$$

Proved.

Hess Law:-

This law was enunciated by Hess, a Russian chemist in 1840, according to which-

“Whether a reaction occurs only in one step or in general steps, the net change in heat energy always remains the same”.

Experimental proof:-

Formation of CO₂.

(i). First method takes place in only one step-



Here, $\Delta H = -94.4\text{k.cal}$

(ii). Second method takes place in two steps-



Here, ΔH for both steps = 94.4k.cals

It is clear from this example that in both methods, amount of heat evolved during this reaction is the same.

Theoretical proof:-

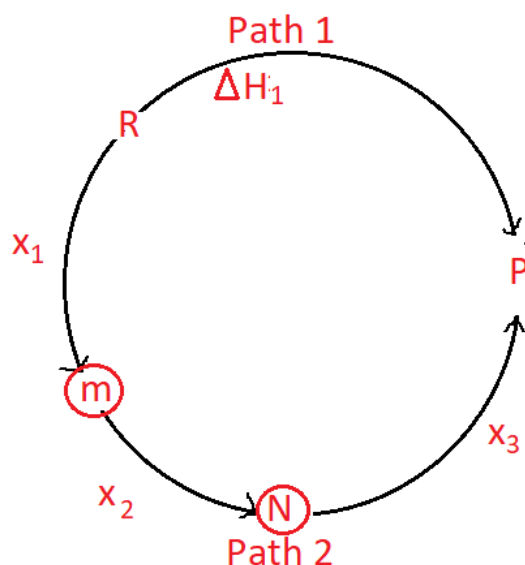
Let us consider a reversible reaction from R to P which occurs in two ways-

(i). In first method, we have only one step and suppose in word process ΔH , heat is evolved.

(ii). In second method, we have three steps and in these steps heat evolved is x_1 , x_2 and x_3

Suppose,

$$x_1 + x_2 + x_3 = \Delta H_2$$



Now, following cases may arise-

If $\Delta H_1 \neq \Delta H_2$, then let us suppose that $\Delta H_1 > \Delta H_2$. If this is the situation then, in connecting from R to P and then from P to R $\Delta H_1 - \Delta H_2$ amount of heat will be evolved. If the process is repeated to many times, a huge amount of energy will be stored which is against the first law of thermodynamics. Therefore, $\Delta H_1 \neq \Delta H_2$.

Similarly, it can be proved that $\Delta H_1 \neq \Delta H_2$

Hence, $\Delta H_1 = \Delta H_2$.

Application of Hess's Law:-

- (1) It is used in determination of bond energy.
- (2) It is used in the determination of heat of formation.
- (3) It is used in the determination of electron affinity.
- (4) It is used in the determination of dissociation of electron.

Kirchhoff's Law:-

According to this law-

“The change in heat of reaction per unit change in temperature is equal to the difference in the heat capacity of product and reactant at constant pressure”.

Thus, Kirchhoff's studied the effect of temperature on heat of reaction and deduced following equation-

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

Where, ΔC_p = Heat capacity of product at constant pressure.
Heat capacity of reactants at constant pressure.

Derivation,

Let us consider following chemical reaction-



Suppose,

Enthalpies of all reactants = H_R .

Enthalpies of all products = H_P .

Then,

$$\text{Heat of reaction, } \Delta H = H_P - H_R \longrightarrow (1)$$

On differentiating this equation (1) with respect to T at constant P we get,

$$\left[\frac{\delta(\Delta H)}{\delta T} \right]_P = \left[\frac{\delta H_P}{\delta T} \right]_P - \left[\frac{\delta H_R}{\delta T} \right]_P \longrightarrow (2)$$

By definition of C_p , we know that,

$$\left[\frac{\delta H_P}{\delta T} \right]_P = C_p \text{ (Product)}$$

$$\left[\frac{\delta H_P}{\delta T} \right]_P = C_p \text{ (Reactant)}$$

On using this definition in equation (2) we get,

$$\left[\frac{\delta\Delta H}{\delta T}\right]_P = C_p (\text{product}) - C_p (\text{Reactant})$$

$$\text{Or, } \left[\frac{\delta\Delta H}{\delta T}\right]_P = \Delta C_p.$$

$$\text{Or, } \delta\Delta H = \Delta C_p \cdot \delta T$$

on integrating this equation, we get,

$$\int_{\Delta H_1}^{\Delta H_2} \delta(\Delta H) = \int_{T_1}^{T_2} \Delta C_p \delta T.$$

Assuming ΔC_p to be independent of temperature-

$$\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1]$$

$$\text{Or, } \boxed{\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p} \longrightarrow (3)$$

However, if the reaction occurs at constant volume, the Kirchoff's law can be written as-

$$\boxed{\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v} \longrightarrow (4)$$

Where,

ΔC_v = Heat capacity at constant volume of product -
Heat capacity of reactants at constant volume.