

# Thermodynamics

Thermodynamics means flow of heat. It deals with change of energy in all physical and chemical processes.

Thermodynamics is mainly based on two principles called 1st law and 2nd law of thermodynamics.

The limitation of the thermodynamics is that it can only apply to matter which is in bulk and not to individual atoms or molecules.

For clear understanding of the thermodynamics the knowledge of some basic terms are important.

**System:** — Any specified portion of the matter which is under observation and separated from the rest of the universe with a boundary.

**Surrounding:** — The rest part of universe which might be in a position to exchange energy and matter with the system is called surrounding.

**Isolated system:** — A system which can't exchange energy as well as matter with its surroundings.

**Closed system:** — A system which can exchange energy but not matter with the surroundings is known as closed system.

**Open system:** — A system which can exchange matter as well as energy with its surrounding is called open system.

**Macroscopic Properties:** — It consists the properties of large numbers of particles such as pressure, volume, temperature, density, viscosity --- etc.

**Homogeneous and heterogeneous system:** —

**Homogeneous system:** — This system consists of only one phase and completely uniform throughout i.e. pure solid, pure liquid or a solution or mixture of gases.

**Heterogeneous system:** — A system which is not uniform throughout is called heterogeneous or a system which consists two or more phases is an heterogeneous system.

**State of a system:** — The state of a system is fixed by its macroscopic properties. When macroscopic properties of a system has definite values then the system is said to be in definite state.

**State Variables:** — Since the state of the system changes with change in any of the macroscopic properties, these properties are called state variables.

**Extensive Properties & Intensive Properties:** —

**Extensive Properties** of a system is that which depends upon the amount of the substance present in the system. i.e. Mass, Volume and Energy.

**Intensive Properties** of a system is that which does not depend upon the amount of the substance present in the system. For example, Pressure, Temperature, viscosity, density and refractive index --- etc.

## Thermodynamic Processes:-

**Isothermal Process:** - When the temperature of the system remains constant during each step of the process, then the process is said to be Isothermal.

**Adiabatic Process:** - A process is said to be adiabatic if no heat enters or leaves the system during any steps of the process. or when the heat of the system remains constant during each step of the process, then the process is said to be Adiabatic Process.

**Isobaric Process:** - When the pressure of the system remains constant during each step of the process, then the process is said to be Isobaric.

**Isochoric Process:** - When volume of the system remains constant during each step of the process, then the process is said to be Isochoric.

### Reversible and Irreversible Process: -

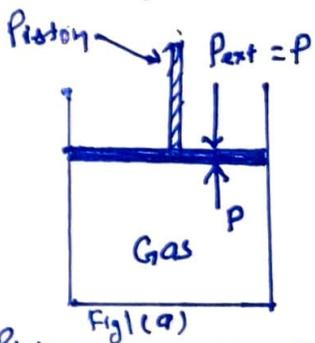
**Reversible Process:** - A process carried out infinitesimally slow is called reversible process.

**Irreversible Process:** - The process which does not take place infinitesimally slowly, is said to be an irreversible process.

A reversible process cannot be realised in practice because it would require infinite time for its completion. So, all the processes occurring in the nature or laboratory are irreversible. Therefore the concept of reversible process is imaginary and theoretical.

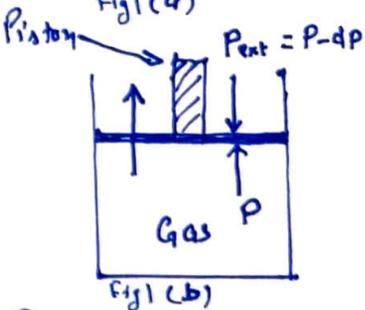
Reversible and irreversible process may be understood by the following example,

Let us consider a cylinder provided with an air-tight, weightless and frictionless piston, containing a certain quantity of a gas. As shown in fig.



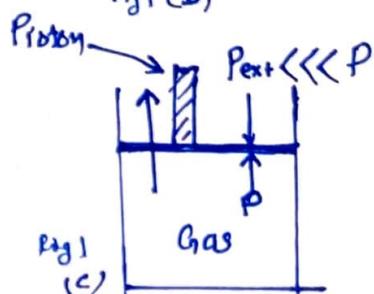
Let the pressure  $P$  on the piston is exactly equal to the pressure of the gas within the cylinder. The piston will neither move downward nor upward and consequently there will be no change in the volume of the gas in fig 1 (a).

Now suppose the pressure on the piston is decreased by an infinitesimally small amount  $dP$ . The pressure on the piston is  $(P - dP)$  infinitesimally smaller than the pressure  $P$  of the gas within the cylinder (Fig. 1 (b)). Hence the piston will move up and the gas will expand infinitesimally small amount.



If the pressure on the piston is kept infinitesimally smaller than the pressure of the gas itself so the expansion of the gas will continue infinitesimally slow i.e. in thermodynamic reversible manner.

If however the pressure on the piston (external pressure) is made much smaller than the pressure of the gas within the cylinder then the gas will expand rapidly. On pushing the piston upward suddenly (Fig 1 (c)) the expansion of the gas occurs irreversibly.



## First Law of Thermodynamics

The first law of thermodynamics states that energy can neither be created nor destroyed, it can be only transformed from one form to another. This law is also known as conservation of energy.

Let us suppose that there is no such equivalence between heat and work. Then it may be possible first time to convert certain amount of heat ( $x$ ) joules into a certain amount of mechanical work and then in the reverse process transformation of the same amount of mechanical work into heat producing ( $y$ ) joules of heat.

where  $y > x$   
Thus the original condition will have been restored, but the heat equivalent to  $(y-x)$  joules will have been created and in this way perpetual motion machine can be created.

But according to human experience there must be equivalence of heat and work. It is well known fact that energy can be created by destruction of mass. Thus these two quantities may be related as

$$E = mc^2 \text{ (Einstein's eqn)}$$

where  $E = \text{energy}$ ,  $m = \text{mass}$  &  $c = \text{velocity}$

The modified law states that the total mass and energy of an isolated system remains constant & the term system explains the ideal gas always

Energy substance is associated with definite amount of energy which depends upon its chemical nature as well as its temp., volume and pressure. This energy is known as intrinsic energy.

The internal energy of a system is a state function it does not depend upon the path, hence change in internal energy depends on its final and initial state so it is exact or perfect differential.

Internal energy is represented by  $U$  or  $E$

Let  $U_A$  be the energy of the system in state A and  $U_B$  be the energy of the system in state B.

$$\therefore \Delta U = U_B - U_A$$

If a system is going under change from state A to state B. Then heat taken by the system is  $q$  and work done is  $w$

$$\therefore \Delta U = q - w$$

If in a given process, the quantity of heat transferred from the surrounding to the system is  $q$  and work done in the process is  $w$  then the change in internal energy  $\Delta U$  is given by

$$\Delta U = q + w$$

If work is done by the surrounding on the system (compression of gas) the  $w$  is taken as (+) positive sign

$$\text{So, } \Delta U = q + w \quad (\text{compression})$$

On the other hand if work is done by the system on the surrounding (expansion of gas)  $w$  is taken as negative (-) sign

$$\text{So, } \Delta U = q - w$$

First law eq<sup>n</sup> ( $\Delta U = q + w$ ) where  $\Delta U$  is a definite quantity. Thus energy, pressure, temperature, volume are state function. On the other hand  $q$  and  $w$  are not state function.

In terms of mathematics we can say that differential of energy  $du$  is an exact differential and heat and work has inexact differentials.

So, the exact differentials can be integrated between the appropriate limits, but it can not be done in case of inexact differentials.

Hence,  $\int_{u_1}^{u_2} du = u_2 - u_1$

But  $\int_{q_1}^{q_2} dq \neq q_2 - q_1$ , and  $\int_{w_1}^{w_2} dw \neq w_2 - w_1$

### Limitations of 1st Law: -

- (1) It gives definite relation between heat absorbed and work done but it puts no restriction of the direction of flow of heat.
- (2) Energy of an isolated system remains constant during specified change of state but it does not tell the reaction or change occurs spontaneously.
- (3) The first law does not indicate whether a transformation of energy would at all occur and if occur to what extent.



## Heat Capacity: —

If the mass of the system is one gram, the heat capacity is called the specific heat of the system.

If the mass of the system is one mole, then the heat capacity is called molar heat capacity and it is denoted by  $C$ .

Thus the molar heat capacity of the system between temperatures  $T_1$  and  $T_2$  will be expressed as

$$C = \frac{q}{(T_2 - T_1)}$$

The heat capacity varies with temperature, hence the true molar heat capacity is defined by the differential equation.

$$C = dq$$

It is known that the molar heat capacity of a gaseous system which is determined at constant volume is different from the molar heat capacity of gaseous system at constant pressure.

In the case of constant volume no external work is done by the system or on the system (i.e.  $w = 0$ ) since there is no change in volume, hence from the first law ( $\Delta U = q + w$ ) eq<sup>n</sup>

$$q = \Delta U$$

$$C_v = \left( \frac{q}{T_2 - T_1} \right)_v = \frac{\Delta U}{(T_2 - T_1)_v} \quad \left\{ \text{on substituting the value of } q = \Delta U \right\}$$

$$C_v = \left( \frac{\Delta U}{\Delta T} \right)_v = \left( \frac{\partial U}{\partial T} \right)_v$$

At constant pressure, there is change of volume and some work is done. Let the volume is increased by  $\Delta V$  and work done is  $w$ .

Then from 1st law eq<sup>n</sup>  $\Delta U = q + w$

$$q = \Delta U - w$$

$$\text{and } C_p = \left( \frac{q}{T_2 - T_1} \right)_p$$

Increase in volume means, the work is done by the system on the surrounding so, by convention  $w$  is negative

$$\text{Hence } w = -P\Delta V$$

$$\therefore q = \Delta U - w \\ = \Delta U + P\Delta V$$

$$\therefore C_p = \left( \frac{q}{T_2 - T_1} \right)_p = \left( \frac{\Delta U + P\Delta V}{T_2 - T_1} \right)_p$$

$$= \left( \frac{\Delta H}{T_2 - T_1} \right)_p$$

$$= \left( \frac{\partial H}{\partial T} \right)_p$$

$$\left[ \because \Delta U + P\Delta V = \Delta H \right]$$

Thus the molar heat capacity  $\left( \frac{\partial H}{\partial T} \right)_p$  of a gaseous system of mass one mole at constant volume is defined as the increase in internal energy of the system per degree rise of temp.

And at const. pressure defined as the increase in enthalpy of the system per degree rise of temperature.

## Relation between $C_p$ and $C_v$

At Constant Volume when a gas is heated then no external work is done by the gas. It means all the heat supplied to the gas is used in increasing its internal energy.

Thus the temperature of one mole of the gas is raised through  $1^\circ\text{C}$  (i.e. from  $T$  to  $T+1$ ), then the increase in its internal energy itself gives the molar heat capacity at constant volume.

However when a gas is heated at constant pressure then there will be increase in its volume. It means the gas will expand and it will do some external work.

Therefore, some extra heat (in addition to the heat required by it to increase the internal energy of its molecules) must be supplied to the gas to enable it to perform this external work.

Hence the molar heat capacity of a gas at constant pressure must be greater than that of the heat capacity at constant volume

$$\text{i.e. } C_p > C_v$$

$$\text{Thus } C_p - C_v = \text{Work done by one mole of the gas in expansion at const. pressure.}$$

We know at const. pressure work done by the gas in expansion  $W = P\Delta V$

$$\text{For 1 mole of ideal gas } PV = RT \quad \text{--- (1)}$$

When the temperature is raised by  $1^\circ\text{C}$  from  $(T)$  to  $(T+1)$  so that the volume is  $V + \Delta V$ ,

then

$$P(V + \Delta V) = R(T+1) \quad \text{--- (2)}$$

On subtracting eq<sup>n</sup> (1) from eq<sup>n</sup> (2) we have

$$P(V + \Delta V) - PV = R(T+1) - RT$$

$$\text{or } PV + P\Delta V - PV = RT + R - RT$$

$$\text{or } P\Delta V = R$$

Thus the work done by one mole of an ideal gas in expansion at constant pressure when heated through  $1^\circ\text{C}$  is equal to  $R$ .

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

So, we can say that the difference between molar heat capacity of a gas at constant pressure ( $C_p$ ) and at constant volume ( $C_v$ ) is equal to gas constant  $R$ .