First Law of Thermodynamics

Thermodynamics – It is the science that discusses the relation of heat to mechanical work. It establishes the equivalence between the workdone and the heat produced. The principle of thermodynamics are very general and give the relation of heat to other forms of energy e.g. electrical, light etc.

Mechanical equivalent of heat:

Whenever work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.

$W \propto H$ or, $\boxed{W = JH}$

where J is a constant known as Joule's mechanical equivalent of heat. In S.I system both W and H are measured in Joules. Therefore, in this system $J = 1$ and therefore $\boxed{W = H}$.

First law of thermodynamics:

Whenever heat is imparted to a body, a part of it is used to increase in internal energy i.e, to rise it's temperature and the rest in doing external work. If δQ is the heat energy absorbed by a system δU the increase in its internal energy and δW the external work done by it, then provided all the quantities are measured in units of work, we have,

$$\delta Q = \delta U + \delta W$$

This equation is known as the first law of thermodynamics.

Differential form of first law of thermodynamics:

When an infinitesimal small amount of heat dQ is added to the system so that it causes an increase dU in internal energy and in addition performs an external work dW, then according to the principle of conservation of energy,

$$dQ = dU + dW$$

This is the differential form of the first law of thermodynamics.

If the pressure remains constant at P and a change in volume dV take place, then $dW = PdV$

$$\boxed{\therefore dQ = dU + PdV}$$

Note – (1) First law is applicable to all states of matter (solid, liquid and gas) and any type of transformation (2) First law gives the existence of internal energy function
(3) First law is based on principle of conservation of energy.
(4) First Law gives the defination of heat as energy.

Physical significance

The first law of thermodynamics is simply the conservation of energy principle in its most general form. It recognises transfer of energy through either work or heat and it includes in the internal energy of the system all form of energy due to ordered as well as disordered motion of the particles of the system.

In all transformation the energy due to heat supplied to the system must be balanced by the external workdone plus the increase in internal energy.

Internal energy :

If we have a certain volume of gas enclosed in a vessel, then the molecules of the gas are in a state of constant random, thermal motion. As such they possess a kinetic energy.

In the case of real gas, the molecules also exert a force of attraction on one another and as a result posses potential energy.

The sum total of the kinetic and potential energies of all the gas molecules taken together is known as internal energy of the gas and denoted as U.

Perfect gas :- For a perfect gas, the molecules of the gas do not exert any force of attraction and as such the potential energy of the molecules is zero.

The internal energy of an ideal (perfect) gas is, therefore equal to the sum total of only the kinetic energies of all the molecules.

The internal energy of an ideal gas at temperature T.

$$\boxed{U = \frac{3}{2} NKT}.$$

where N is the total number of molecules of the gas and K the Boltzmann constant.

For cyclic process total change of internal energy must be zero. $\oint dU = 0$.

Hence 1st law for cyclic process ⇒ $\boxed{\oint dq = \oint dW}$

⇒ 1160 K.

Specific heat :- The amount of heat needed to rise the temperature of one gram of a substance by one degree, usually measured in jouls per kilogram per kelvin.

Two specific heats of a gas :

When a gas is heated, ordinarily there is an increase in volume as well as pressure in addition to the rise of temperature. Either the volume or the pressure may be kept constant. Therefore a gas has two specific heats.

(i) specific heat at constant volume, and

(ii) specific heat at constant pressure.

If dQ is the amount of heat required to rise the temperature of a unit mass of the gas through $dT°C$, keeping the volume constant, then, specific heat at constant volume $C_V = \left(\frac{dQ}{dT}\right)_V$.

If dQ is the amount of heat required to rise the temperature of a unit mass of the gas through $dT°C$ keeping the pressure const, then, specific heat at constant pressure $C_P = \left(\frac{dQ}{dT}\right)_P$.

Difference between two specific heats :

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V$$

From 1st law of thermodynamics,

$$dQ = dU + P\,dV$$

Since, $V =$ const, so, $dV = 0$ $\quad \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$

or, $\boxed{dU = C_V\, dT}$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad -(1)$$

Again $C_P = \left(\frac{\partial Q}{\partial T}\right)_P$ $\Rightarrow$ From, $dQ = dU + P\,dV \Rightarrow \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$

$$\therefore C_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P \rightarrow (2)$$

$$C_P - C_V = \left(\frac{\partial Q}{\partial T}\right)_P - \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V \rightarrow (3)$$

Again $U = \phi(V, T)$

Diff^n partially,

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \rightarrow (4)$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

Putting the value of eq^n (4) in eq^n (3)

$$C_P - C_V = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \cancel{\left(\frac{\partial U}{\partial T}\right)_V} + P\left(\frac{\partial V}{\partial T}\right)_P - \cancel{\left(\frac{\partial U}{\partial T}\right)_V}$$

$$\boxed{C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P}$$