Unit

6

Thermodynamics

- **Thermodynamics** is a branch of science which deals with the study of interconversion of different forms of energies and their quantitative relationships.

INTERNAL ENERGY

- The total energy stored in a substance (or a system) is called its internal energy. It is the sum of various energies associated with atoms and molecules such as translational energy (E_t), vibrational energy (E_v), rotational energy (E_r), potential energy (E_p), electronic energy (E_e), nuclear energy (E_n), chemical energy (E_c), etc.

  Thus U or $E = E_t + E_v + E_r + E_p + E_e + E_n + E_c$
- It is a state function whose absolute value can not be determined because all kind of energies associated with it can not be measured. However change in internal energy (ΔU) can be calculated.

  $\Delta U = U_2 - U_1$ or $\Delta U = U_{\text{product}} - U_{\text{reactant}}$

  Where U_2 and U_1 represent the internal energy of final and initial state respectively.

FIRST LAW OF THERMODYNAMICS

- It is a law of conservation of energy which states that energy can neither be created nor destroyed, although it can be converted from one form to another. This obviously means that total energy of the universe remains constant.

  Mathematically : ΔE or $\Delta U = q + W$ or $q = \Delta U - W$
  - If W is work of expansion *i.e.*, $W = -P\Delta V$ then $\Delta U = q - P\Delta V$ or $q = \Delta U + P\Delta V$
  - For isothermal irreversible expansion $\Delta U = 0$ thus $q = -W = P\Delta V$
  - For isothermal reversible expansion $\Delta U = 0$ thus

    $$q = -W = 2.303\,nRT\,\log\frac{V_2}{V_1}$$
  - For adiabatic processes, $q = 0$ thus $\Delta U = W_{\text{adiabatic}}$

    We know $\frac{dU}{dT} = C_V \Rightarrow dU = C_V dT$

    Thus $W_{\text{adiabatic}} = C_V dT = C_V(T_2 - T_1)$
  - For isochoric process, $\Delta V = 0$, thus $q = \Delta U$

- **Graphical representation of thermodynamic processes**

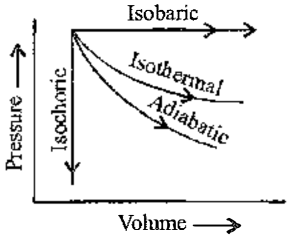

Illustration 1

10 g of argon gas is compressed isothermally and reversibly at a temperature of 27° C from 10 litre to 5 litre. Calculated q, W and ΔU for this process.

($R = 2.0$ cal K^{-1} mol^{-1}, atomic weight of Argon = 40)

Soln.:

$$W_{\text{iso, rev}} = -2.303\,nRT\log\frac{V_2}{V_1} = -2.303\,nRT\log\frac{5}{10}$$

$$= -2.303 \times \frac{10}{40} \times 2 \times 300\log\frac{5}{10} = 103.9 \text{ cal.}$$

For isothermal process $\Delta U = 0$

From 1st law of thermodynamics, $\Delta U = q + W$

$\therefore\; q = -W = -103.9$ cal

ENTHALPY

- Total heat content of the system at constant pressure is known as its enthalpy.

  $H = U + PV$

  If H_2 is the enthalpy in final state and H_1 in initial state, then

  $\Delta H = H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1)$

  $\boxed{\Delta H = \Delta U + P\Delta V}$
- Enthalpy change represents the heat absorbed or evolved by the system at constant pressure. It is a state function.
- **Sign convention :** For exothermic reaction (*i.e.*, heat released during the reaction) ΔH is negative *i.e.*, $\Delta H < 0$. Whereas for endothermic reaction (*i.e.*, heat absorbed during the reaction), ΔH is positive *i.e.*, $\Delta H > 0$.
- **Relationship between ΔH and ΔU**

  We know that $\Delta H = \Delta U + P\Delta V$

  ΔV is the change in volume *i.e.*, $\Delta V = V_2 - V_1$