

- It's the law of conservation of energy

□ **The energy of an isolated system remains constant. Whenever a quantity of energy (some form) disappears, an exactly equivalent quantity of energy (some other form) must make an appearance.**

➤ **Heat (q) and work (w)** are equivalent ways of changing the internal energy of a system

→ Example:

- If a weight has been raised/lowered in the surroundings, transfer of energy happens by doing the work.
- If ice has melted in the surroundings, it indicated transfer of energy as heat.

➤ For a system, if w = work done on a system, q
= energy transferred as heat to a system &
 ΔU = resulting change in internal energy

$$\Delta U = q + w$$

The sign of w and q:

✓ **+ve** if energy is transferred to the system as work/heat

✓ **-ve** if energy is lost from the system.

Therefore,

***change in internal energy* (ΔU) of a system = heat added to the system (q) - the work done *by* the system (w)**

$$\Delta U = q - w$$

- If the change of a system is brought about at constant pressure, there will be change in volume.

V_i = volume of initial state, V_f = volume of final state.

Work done by the system, $w = -P (V_f - V_i)$

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

$$\text{or, } \Delta U = q - P (V_f - V_i)$$

$$\Rightarrow U_f - U_i = q - P (V_f - V_i)$$

$$\Rightarrow (U_f + PV_f) - (U_i + PV_i) = q$$

- The quantity (**$U + PV$**) is called the **enthalpy (H)** of the system

$$\Rightarrow H_f - H_i = q$$

$$\Delta U = \Delta H - P\Delta V$$

or, $\Delta H = \Delta U + P\Delta V$

- Heat capacity (**C**) of a system b/n any two temperatures – the quantity of heat (q) required to raise the temperature of the system from the lower temperature (T_1) to the higher temperature (T_2) divided by the temperature difference.

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

- ☺ If mass of the system is 1 g,
the heat capacity is called the **specific heat of the system**
- ☺ For 1 mol of substance,
the heat capacity is termed as '**molar heat capacity**'

- Molar heat capacity varies with temperature

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

- **Molar heat capacity at constant volume**

@ constant volume $w = 0$ & $\Delta U = q$

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

❑ Molar heat capacity at constant pressure (C_p)

$$\Delta U = q + w$$

@ constant pressure,
there is change in volume
& some work is done

$$\Delta U = q - P (V_f - V_i)$$

or, $q = \Delta U + p\Delta V$



As quantity ($U + PV$) is the
enthalpy (H) of the system

\Rightarrow

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

❑ Relationship between C_p & C_v

For a system, $\Delta H = \Delta U + \Delta(PV)$

$$\text{or, } \frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + \frac{\Delta(PV)}{\Delta T}$$

$$\text{or, } C_p = C_v + \frac{\Delta(PV)}{\Delta T}$$

- For ideal gas, $PV = RT$ (for 1 mole)

$$\Delta(PV) = R \Delta T$$

$$C_p = C_v + \frac{R\Delta(T)}{\Delta T} \quad \text{or, } C_p = C_v + R$$

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

$$C_v = \frac{3}{2} R \quad (\text{For monoatomic ideal gas})$$

$$C_p = \frac{5}{2} R \quad (\text{For monoatomic ideal gas})$$

$$\text{Heat capacity ratio, } \gamma = \frac{C_p}{C_v} = \frac{5}{3} \text{ for a monoatomic ideal gas}$$

➤ Isothermal Process (constant temperature)

- In an isothermal process, the temperature stays constant, so the **pressure and volume** are **inversely proportional** to one another

⇒ **For an ideal gas,**

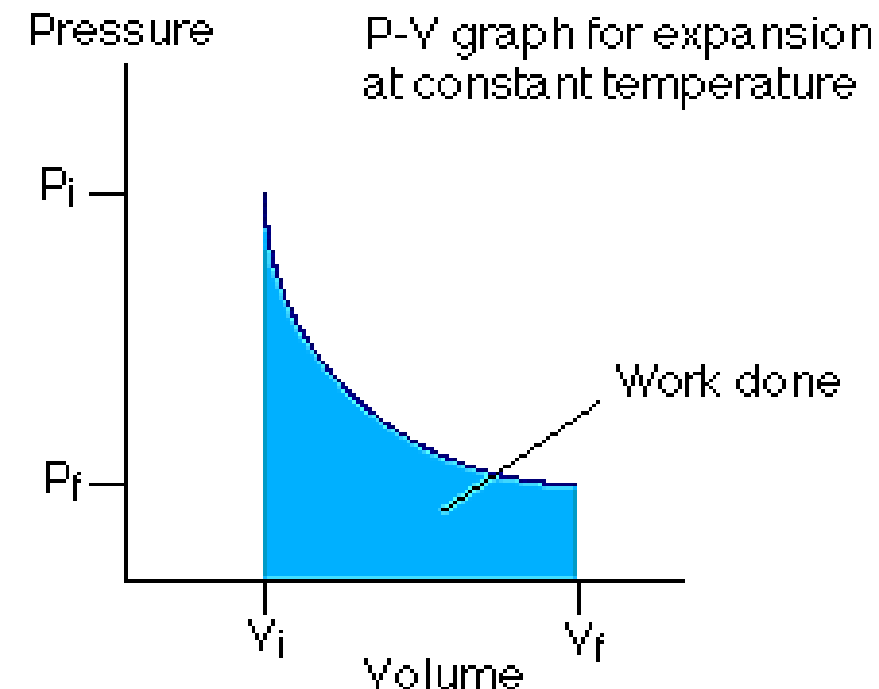
The internal energy (U) \propto Temperature (T)

if $T = \text{fixed}$, $\Delta U = 0$ (according to 1st law, which deals with ΔU)

$$\text{As, } \Delta U = q - w = 0$$

$$\Rightarrow q = w$$

Magnitude of w depends on whether the expansion is reversible or irreversible.



- If the **system does work**, the energy comes from **heat flowing into the system from the surrounding**
- if **work is done on the system**, heat flows **out of the system to the surrounding**.