Heat Capacity — It is the quantity of heat that must be supplied or removed by the body to change its temperature by one kelvin. It is an extensive property.

Mathematically, Heat capacity of a system is defined as,

$$C = \lim_{\Delta T \to 0} \frac{q}{\Delta T} = \frac{dq}{dT}$$

It is a path dependent variable. Heat capacity of a body is expressed as JK^{-1}.

Heat capacity can be classified into following types —

1) **Heat capacity at constant pressure** —

In this process the external pressure is constant. It is expressed as C_p.

Heat capacity at constant pressure (C_p) is given by,

$$C_p = \left(\frac{dq}{dT}\right)_P \quad \text{---} (1)$$

from Enthalpy, we know,

$$H = U + PV$$

where, H = Enthalpy
U = Internal Energy
P = Pressure
V = Volume

or, $dH = dU + PdV + VdP$

Here, at Const Pressure, $VdP = 0$.

$\therefore dH_p = dU_p + PdV$

or, $dH_p = dq_p$ [from 1st law of thermodynamics, $dq_p = dU + PdV$]

$$\therefore \left(\frac{dH}{dT}\right)_P = \left(\frac{dq}{dT}\right)_P$$

$$\therefore \boxed{C_p = \left(\frac{dH}{dT}\right)_P} \quad [\because \text{using} - (1)]$$

2) Heat capacity at constant volume —

In this process of heat capacity the system is in at constant volume and it is expressed as C_V.

Heat capacity at constant volume is given by,

$$C_V = \left(\frac{dq}{dT}\right)_V \quad --- (1)$$

from 1st law of Thermodynamics, we know,

$$dq = dU + PdV$$

at const volume, $PdV = 0$.

$$\therefore (dq)_V = (dU)_V$$

or, $$\left(\frac{dq}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

or, $$\boxed{C_V = \left(\frac{dU}{dT}\right)_V} \quad [\text{using} - (1)]$$

Relation between C_p and C_V —

- $C_p - C_V = nR$

$\because$ We know,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_P \quad \text{and} \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\therefore C_p - C_V = \left(\frac{dU}{dT}\right)_P - \left(\frac{dU}{dT}\right)_V$$

Now, using Enthalpy formula, here, we get; $[H = U + PV]$

or $$C_p - C_V = \left(\frac{dU}{\partial T}\right)_P + P\left(\frac{dV}{dT}\right) - \left(\frac{dU}{dT}\right)_V \quad --- (1)$$

Internal Energy is a function of volume and temperature.

$$\therefore \; U = f(V, T)$$

or, $$dU = \left(\frac{\partial U}{\partial T}\right)_V \partial T + \left(\frac{\partial U}{\partial V}\right)_T \partial V$$

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

At constant pressure,

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad --- (2)$$

Now, putting the value of (2) in (1), we get,

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

$$= P\left(\frac{\partial V}{\partial T}\right)_P \left[1 + \frac{1}{P}\left(\frac{\partial U}{\partial V}\right)_T\right] \quad --- (3)$$

According to thermodynamic equation of state,

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Substituting $\left(\frac{\partial U}{\partial V}\right)_T$ in eqn (3), we get,

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad --- (4)$$

For an ideal gas, $PV = nRT$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad \text{and} \quad \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad — (5)$$

Putting the value of (5) in (4) we get,

$$C_P - C_V = T \times \frac{nR}{V} \times \frac{nR}{P} = \frac{nR \times nR \times T}{nRT} = nR$$

$$\therefore \; \boxed{C_P - C_V = nR}$$

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