

⇒ Molar heat capacity at constant pressure is given by

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

and that at constant volume by the relation

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

The difference between  $C_p$  and  $C_v$  is

$$C_p - C_v = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \text{ ----- (1)}$$

Again,  $H = U + pV$ , where  $H$  is enthalpy,  $U$  is internal energy,  $p$  = pressure and  $V$  is the volume. Hence equation (1) becomes

$$C_p - C_v = \left[ \frac{\partial (U + pV)}{\partial T} \right]_p - \left( \frac{\partial U}{\partial T} \right)_v$$

$$= \left( \frac{\partial U}{\partial T} \right)_p + p \left( \frac{\partial V}{\partial T} \right)_p - \left( \frac{\partial U}{\partial T} \right)_v \text{ ----- (2)}$$

since  $U = f(V, T)$ ;  $T = \text{temperature}$ .

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

dividing by  $dT$  at constant pressure, we get

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

substituting the value of  $\left(\frac{\partial U}{\partial T}\right)_P$  in equation-②, we get

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

$$\therefore \boxed{C_P - C_V = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P} \text{ --- ③}$$

This is the general relation between  $C_P$  and  $C_V$ . This equation is applicable for any materials i.e., solid, liquid and gas (ideal and real).