

Enthalpy (H) $\Rightarrow$ Enthalpy is defined as the total heat content of a system.

$$H = U + PV$$

If is a state function and an extensive property.

Suppose a system containing ideal gas has enthalpy H_1 and after changing its volume from V_1 to V_2 the enthalpy becomes H_2 .

Initially

$$H_1 = U_1 + PV_1$$

Finally

$$H_2 = U_2 + PV_2$$

$$H_2 - H_1 = U_2 - U_1 + P(V_2 - V_1)$$

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

For an ideal gas, $PV = nRT$

$$\Delta H = \Delta U + \Delta nRT \quad (\because P\Delta V = \Delta nRT)$$

From first law

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

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

$$\Delta H = q - \cancel{P\Delta V} + \cancel{P\Delta V}$$

$$\Delta H = (q)_p \quad (\text{at constant pressure})$$

If $\Delta H = -ve$ the reaction is exothermic

If $\Delta H = +ve$ the reaction is endothermic.

Heat capacity at constant volume (C_v) and constant pressure (C_p) $\Rightarrow$

$$C_v = \frac{q_v}{\Delta T}$$

From first law of thermodynamics

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

at constant volume $\Delta V = 0$

$$\Delta U = q_v$$

$$\boxed{C_v = \frac{\Delta U}{\Delta T}}$$

for n moles, $\boxed{\Delta U = n \bar{C}_v \Delta T}$

$\bar{C}_v \rightarrow$ molar heat capacity at constant volume.

$$C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T}$$

$$\boxed{\Delta H = n \bar{C}_p \Delta T}$$

Relation between C_p and $C_v \Rightarrow$

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

$$= \left\{ \frac{\partial (U + PV)}{\partial T} \right\}_p - \left(\frac{\partial U}{\partial T} \right)_v$$

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

$$U = U(V, T)$$

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

dividing by δT at constant pressure (P).

(1)

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

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

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

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

for an ideal gas

$$\left(\frac{\delta U}{\delta V}\right)_T = 0$$

$$\left(\frac{\delta H}{\delta P}\right)_T = 0$$

$$C_P - C_V = P \left(\frac{\delta V}{\delta T}\right)_P$$

$$PV = nRT$$

$$\left(\frac{\delta V}{\delta T}\right)_P = \frac{nR}{P}$$

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

$$C_P - C_V = nR$$

for 1 mole i.e. $n=1$

$$\boxed{C_P - C_V = R}$$

$$C_P > C_V$$

