

TDC-I(H) & TDC-II(Sub.)

Relation between C_p & C_v

For 1 mole of Gas, The rise of 1°C Temperature at constant volume results Increase in internal Energy. Such increase in internal Energy is molar heat Capacity (C_v). At constant pressure molar heat Capacity (C_p) is greater than C_v and The difference

$C_p - C_v =$ work done by one mole of a gas during expansion at constant pressure by the rise of 1°C Temperature

Since $PV = RT$
for 1 mole

$$P(V + \Delta V) = R(T + 1)$$

$$PV + P\Delta V = RT + R$$

$$P\Delta V = R$$

Hence $C_p - C_v = R$ This is required relation b/w C_p & C_v

Also $H = U + PV$

$$\frac{dH}{dT} = \frac{dU}{dT} + R \Rightarrow C_p - C_v = R$$

For
TDC-I (H)
TDC-II (Sub.)

Kirchhoff's Equation

The enthalpy change of any process varies with temperature. So Kirchhoff's Equation is regarding the variation of ΔH of a reaction with temperature at constant pressure for a chemical reaction



$$\Delta H_{\text{reaction}} = \sum H_{\text{product}} - \sum H_{\text{reactant}}$$

$$\Delta H_r = (cH_c + dH_d) - (aH_a + bH_b)$$

Differentiating with respect to temperature keeping pressure constant, we have

$$\left[\frac{\delta(\Delta H)}{\delta T} \right]_p = c \left(\frac{\delta H_c}{\delta T} \right)_p + d \left(\frac{\delta H_d}{\delta T} \right)_p - a \left(\frac{\delta H_a}{\delta T} \right)_p - b \left(\frac{\delta H_b}{\delta T} \right)_p$$

$$= c C_{p,c} + d C_{p,d} - b C_{p,b} - a C_{p,a}$$

$$= \Delta C_p$$

$$\left[\because C_p = \left(\frac{\delta H}{\delta T} \right)_p \right]$$

$$d(\Delta H_r) = \Delta C_p dT$$

If ΔH_1 & ΔH_2 be the enthalpy change of reaction at T_1 & T_2 — temperature

Then Integrating both sides

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p \int_{T_1}^{T_2} dT$$

$$\Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1)$$

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta_r C_p = \text{Sum of heat capacity of products} - \text{Sum of heat capacity of reactant at constant pressure.}$$

This Equation is regarded as Kirchhoff's Equation

At Constant Volume

$$d(\Delta U) = \Delta_r C_v dT$$
$$\int_{\Delta U_1}^{\Delta U_2} d(\Delta U) = \Delta_r C_v \int_{T_1}^{T_2} dT$$

$$\Delta U_2 - \Delta U_1 = \Delta_r C_v (T_2 - T_1)$$

$$\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta_r C_v$$

difference of molar heat capacity at constant volume of product and reactant