* Kirchoff's Law :-

The enthalpy of any process, whether physical or chemical, varies with temperature. The exact influence of temperature can be as follows:

Let us consider a reaction —

$$aA + bB \longrightarrow cC + dD$$

The change in enthalpy —

$$\Delta H = \sum H_P - \sum H_R$$

$$\Delta H = (cH_C + dH_D) - (aH_A + bH_B) \quad \text{——— (1)}$$

On differentiating it wrt temperature, keeping pressure constant.

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = c\left(\frac{\partial H_C}{\partial T}\right)_P + d\left(\frac{\partial H_D}{\partial T}\right)_P - a\left(\frac{\partial H_A}{\partial T}\right)_P - b\left(\frac{\partial H_B}{\partial T}\right)_P$$

$$= cC_{P,C} + dC_{P,D} - aC_{P,A} - bC_{P,B}$$

$$= \Delta C_P \quad \text{——— (2)}$$

Where ΔC_P = (Sum of heat capacities of Product) − (Sum of heat capacities of Reactant)

eqn — (2) is called Kirchoff's equation.

It state that —

"The variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_P of the system."

Since,

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_P = \Delta C_p$$

or $d(\Delta H) = \Delta C_p dT$ ——— (3)

and the enthalpy of reaction at constant volume is given by -

$$\left[\frac{\partial(\Delta U)}{\partial T}\right]_V = \Delta C_v$$

or $d(\Delta U) = \Delta C_v dT$ ——— (4)

If the temperature range of interest is small then eqs - (3) & (4) can be easily intigrated by assuming that the heat capacities are independent of temperature.

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

or $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$ ——— (5)

Similarly,

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

or $\Delta U_2 - \Delta U_1 = \Delta C_v (T_2 - T_1)$ ——— (6)

However, the temperature range is not to small, then the enthalpy of reaction at a far higher temperature. The constancy of heat capacities is no longer a valid assumption and we must express -

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the heat capacity as a function of temperature before carrying out the intigration. It is convinent to express the heat capacity as a power series in T.

$$C_p = \alpha + \beta T + \gamma T^2$$

where α, β & γ are constants for a given speises.

Hence,

$$\Delta C_p = [c\alpha_C + d\alpha_D] - [a\alpha_A + b\alpha_B] + [c\beta_C + d\beta_D] - [a\beta_A + b\beta_B]$$

$$T + \ldots$$

$$= \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \quad \text{—— (7)}$$

on substituting eqs (7) in eqs (3) and intigrating —

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2)\, dT$$

or $$\Delta H_2 - \Delta H_1 = \Delta\alpha (T_2 - T_1) + \frac{1}{2}\Delta\beta (T_2^2 - T_1^2) + \frac{1}{3}\Delta\gamma (T_2^3 - T_1^3)$$

$$\text{—— (8)}$$

eqs (8) is called the intigrated Kirchoff's equation.

From

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