

\* 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 —



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  $\Delta C_p = (\text{Sum of heat capacities of Product}) - (\text{Sum of heat capacities of Reactant})$

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

It state that —

"The variation of  $\Delta H$  of a reaction with temperature at constant pressure is equal to  $\Delta C_p$  of the system."

Since,

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

$$\cong d(\Delta H) = \Delta C_p dT \quad \text{--- (3)}$$

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

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

$$\cong d(\Delta U) = \Delta C_v dT \quad \text{--- (4)}$$

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

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

$$\cong \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1) \quad \text{--- (5)}$$

Similarly,

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

$$\cong \Delta U_2 - \Delta U_1 = \Delta C_v (T_2 - T_1) \quad \text{--- (6)}$$

However, the temperature range is not too 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 -

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

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

where  $\alpha$ ,  $\beta$  &  $\gamma$  are constants for a given species.

Hence,

$$\Delta C_p = [c\alpha_c + d\alpha_d] - [a\alpha_a + b\alpha_b] + [c\beta_c + d\beta_d] - [a\beta_a + b\beta_b]$$

$$T + \dots$$

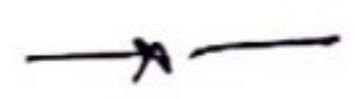
$$= \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \quad \text{--- (7)}$$

on substituting eq<sup>n</sup> (7) in eq<sup>n</sup> (3) ~~and~~ and integrating -

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

$$\Delta H_2 - \Delta H_1 = \Delta\alpha (T_2 - T_1) + \frac{1}{2} \Delta\beta (T_2^2 - T_1^2) + \frac{1}{3} \Delta\gamma (T_2^3 - T_1^3) \quad \text{--- (8)}$$

eq<sup>n</sup> (8) is called the integrated Kirchoff's equation.



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