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# Physical Chemistry - 20

## Revision of Kirchhoff's law

Entropy of a reaction varies with temperature and its variation with the temp.



$$H_1 = x_1 H_{A1} + x_2 H_{B1} \quad \text{--- (for } H_1)$$

$$H_2 = y_1 H_{C1} \quad \text{(for } H_2)$$

$$\Delta H = H_2 - H_1 = y_1 H_{C1} - x_1 H_{A1} - x_2 H_{B1} \quad \text{--- (1)}$$

$$\Delta E = E_2 - E_1 = y_1 E_{C1} - x_1 E_{A1} - x_2 E_{B1} \quad \text{--- (2)}$$

Differentiating w.r.t temp. at constant Vol. & Press.

We deduced following eqs.

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \& \quad C_v = \left( \frac{\partial E}{\partial T} \right)_v$$

At last it is to be seen that integrating the deduced different

derived eqs. we get.

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

Similarly for (2)

$$\int_{E_1}^{E_2} d(E) = \int_{T_1}^{T_2} C_v dT$$

Variation of Enthalpy of reaction with temperature  
ie., Kirchoff's equation: Enthalpy of reaction, in  
general, varies with temperature and its variation  
with temperature can be deduced as follows:

Integrating eq. (5) & (6) between proper limits, we have,

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

Assuming  $\Delta C_p$  to be independent of temperature, we get. ~~eqn (7)~~  $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$  — (7)

Where  $\Delta H_2$  and  $\Delta H_1$  are the enthalpies of reactions at constant pressure at temperature  $T_2$  &  $T_1$ , respectively.

Integrating equation (6) between proper limits, we get.

$$\int_{E_1}^{E_2} d(\Delta E) = \int_{T_1}^{T_2} \Delta C_v \cdot dT$$

$$\Delta E = \Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \cdot dT$$

Assuming  $\Delta C_v$  to be independent of temperature, we get  $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$  — (8)

where  $\Delta E_2$  and  $\Delta E_1$  are the enthalpies of reaction at constant volume, at temperature  $T_2$  and  $T_1$ , respectively.

Kirchoff's law is valid for physical and chemical changes and is independent of nature of and complexity of the systems.