[illegible]

[illegible] : Physical Chemistry [illegible]

[illegible] : Chemical Equilibrium

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] equation [illegible]

$\Delta G^\circ = -2.303\,RT \log K_p$

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] equilibrium.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible] proceed almost to completion.

Combination of Chemical Equilibrium :-

[illegible]

[illegible]

$$K_1 = \frac{[illegible]}{[illegible]} \qquad K_2 = \frac{[illegible]}{[illegible]} \qquad K_3 = \frac{[illegible]}{[illegible]}$$

Multiplying K_1 and K_2 we get

$$K_1 \times K_2 = \frac{[illegible]}{[illegible]} \times \frac{[illegible]}{[illegible]} = \frac{[illegible]}{[illegible]} = K_3$$

or $K_3 = K_1 \times K_2$ —— (B)

Remark :- [illegible]

[illegible]

$$K_1 \times K_2 = \frac{[illegible]}{[illegible]} \times \frac{[illegible]}{[illegible]} = \frac{[illegible]}{[illegible]} = K_3$$

By using equation (B) it is possible to determine the equilibrium constant for a reaction which can not be obtained by direct measurement.

Variation of Equilibrium Constant with temperature :- (van't Hoff Equation)

Equilibrium constant of a reaction [illegible] [illegible]

Change in the value of equilibrium constant with change in temperature. It can be deduced thermodynamically as follows.

In the thermodynamic derivation of equilibrium constant [illegible]

$$\Delta G^\circ = -RT \ln K_p$$

or $\ln K_p = -\frac{\Delta G^\circ}{RT}$ — (1)

Differentiating this equation with respect to temp at constant pressure we get

$$\frac{d \ln K_p}{dT} = -\frac{1}{R}\left[\frac{d(\Delta G^\circ/T)}{dT}\right]_p$$ — (2)

But from Gibbs-Helmholtz equation for a reaction in the standard state we have

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ}{T^2}$$ — (3)

So equation (2) becomes

$$\frac{d \ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2}$$ — (4)

[illegible]

[illegible] equation (4) [illegible] written as

$$\frac{d \ln K_p^\circ}{dT} = \frac{\Delta H^\circ}{RT^2}$$ — (5)

This equation is known as van't Hoff equation where ΔH° is the enthalpy change of the reaction at constant pressure when all the reactants and products are in their standard state.

It can be shown that the enthalpy change [illegible] with change in [illegible] of the reactants or products. [illegible] may be replaced by [illegible] equation (5) becomes

$$\frac{d \ln K_p}{dT} = \frac{\Delta H}{RT^2}$$ — (6)

Integrating equation (9) we get

$$\ln K_p = -\frac{\Delta H}{RT} + C$$

or $$\log K_p = -\frac{\Delta H}{2.303RT} + C \quad \text{--- (10)}$$

where C is integration constant.

When a graph of $\log K_p$ against $\frac{1}{T}$ is plotted we get straight line having slope equal to $-\frac{\Delta H}{2.303R}$ as shown below:

From the graph it is clear that

(a) For exothermic reaction ΔH is negative and K_p decreases with increase in temperature.

(b) For endothermic reaction ΔH is positive and K_p increases with increase in temperature.

Equation (9) can also be integrated between the limits K_{p_1} at temperature T_1 to K_{p_2} at temperature T_2 as

$$\int_{K_{p_1}}^{K_{p_2}} d(\ln K_p) = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2}\, dT$$

or $$\ln \frac{K_{p_2}}{K_{p_1}} = -\frac{\Delta H}{R}\left[\frac{1}{T}\right]_{T_1}^{T_2}$$

$$= -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or $$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{--- (11)}$$

or $$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \quad \text{--- (12)}$$

From this equation the heat of reaction can be determined if the values of equilibrium constants K_{p_1} and K_{p_2} at temperatures T_1 and T_2 are known and vice versa.

van't Hoff Equation in Terms of K_c :-

We know that K_p and K_c are related to each other by the relation

$$K_p = K_c (RT)^{\Delta n}$$

Taking logarithm we get

$$\ln K_p = \ln K_c + \Delta n \ln RT$$

Differentiating with respect to temperature, we get

$$\frac{d(\ln K_p)}{dT} = \frac{d(\ln K_c)}{dT} + \frac{\Delta n}{T}$$

or $$\frac{d(\ln K_c)}{dT} = \frac{d(\ln K_p)}{dT} - \frac{\Delta n}{T}$$

But from equation (iii) we know $\frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}$ and on putting this value in above equation we get

$$\frac{d(\ln K_c)}{dT} = \frac{\Delta H}{RT^2} - \frac{\Delta n}{T}$$

or $$\frac{d(\ln K_c)}{dT} = \frac{\Delta H - \Delta n RT}{RT^2}$$

But we know that $\Delta E = \Delta H - \Delta n RT$ therefore

$$\frac{d(\ln K_c)}{dT} = \frac{\Delta E}{RT^2} \quad \text{---- (iv)}$$

Where ΔE is the heat of reaction at constant volume. This equation (equation (iv)) can be applied in the same manner as equation (iii). Both equations will be identical only when [illegible] $\Delta n = 0$ and $K_p = K_c$.

To be continued......