

Chemical Equilibrium Part III (1)

Relation between the equilibrium constants K_p , K_c and

K_x .

K_p , K_c and K_x are the equilibrium constant of a reaction in terms of ~~concentration~~: partial pressure, concentration and mole fraction respectively.

Relation between K_p and K_c for reaction involving ideal

gas.

For a general reaction:



The equilibrium constant in terms of concentration (mole L^{-1})

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} \rightarrow (1)$$

If the reactants and products are in gaseous form, then the concentration term can be replaced by partial pressure.

The equilibrium constant K_p is written as

$$K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b} \rightarrow (2)$$

For an ideal gas $Pv = nRT$

$$P = \frac{n}{V} RT$$

$P = CRT$ where C is the molar concentration.

Now, we can write

$$P_M = C_M RT \quad P_N = C_N RT, \quad P_A = C_A RT \quad \text{and}$$

$$P_B = C_B RT.$$

Putting the value in eqnⁿ (2), we get

$$K_p = \frac{(C_M RT)^m (C_N RT)^n}{(C_A RT)^a (C_B RT)^b}$$

(2)

$$\text{Or } K_p = \frac{C_M^m C_N^n (RT)^m (RT)^n}{C_A^a C_B^b (RT)^a (RT)^b}$$

$$K_p = \frac{C_M^m C_N^n (RT)^{m+n}}{C_A^a C_B^b (RT)^{a+b}}$$

$$K_p = K_c (RT)^{\Delta n_g} \rightarrow (3)$$

$$\text{Where } \Delta n_g = (m+n) - (a+b)$$

$$= (\text{Sum of moles of Product}) - (\text{Sum of moles of reactant})$$

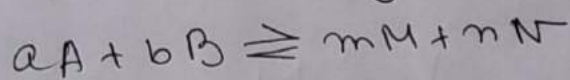
Relation between K_p and K_x .

The partial pressure of a gas in an ideal gaseous mixture is ~~related~~ related to the total pressure P according to Dalton's law of partial pressure as

$$p = x P \rightarrow (4)$$

where p is the partial pressure of a component in the mixture, P is the total pressure of the mixture, x is the mole fraction of that particular component in the mixture.

Let us consider a general reaction



The equilibrium constant in terms of concentration (mole L^{-1}).

$$K_c = \frac{C_M^m C_N^n}{C_A^a C_B^b}$$

If both reactants and products are gaseous

then

$$K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b}$$

(3)

From equⁿ (4)

$$K_p = \frac{(x_M P)^m (x_N P)^n}{(x_A P)^a (x_B P)^b}$$

$$K_p = \frac{(x_M)^m (x_N)^n P^m P^n}{(x_A)^a (x_B)^b P^a P^b}$$

$$K_p = \frac{(x_M)^m (x_N)^n}{(x_A)^a (x_B)^b} \frac{P^{m+n}}{P^{a+b}}$$

$$K_p = K_x (P)^{\Delta n_g} \rightarrow (5)$$

From equⁿ (3) and (5)

$$K_p = K_c (RT)^{\Delta n_g} = K_x (P)^{\Delta n_g}$$

When $\Delta n = 0$, i.e. $(m+n) = (a+b)$,

i.e. No^t of total number ^{of moles} of reactants and the products are equal

then $K_p = K_c = K_x$.

— x — .

Temperature and pressure - dependence of the equilibrium constants.

① Effect of temperature on equilibrium constant:

(Vant Hoff equation or Vant Hoff isochore)

The effect of temperature of chemical equilibrium can be determined by using thermodynamics. when the reactants and products are gaseous and also in the standard state, the relation between ~~the~~ the free energy

(1)

and equilibrium constant can be given by

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

Differentiating eqnⁿ (1), w.r. to T at constant pressure, we get.

$$\left[\frac{d(\Delta G^{\circ})}{dT} \right]_p = - \left(R \ln K_p \frac{dT}{dT} + RT \frac{d \ln K_p}{dT} \right)$$

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

Multiplying eqnⁿ (2) by T

$$T \left[\frac{d(\Delta G^{\circ})}{dT} \right]_p = -RT \ln K_p - RT^2 \left(\frac{d \ln K_p}{dT} \right) \rightarrow (3)$$

From eqnⁿ (1) & (2)

$$T \left(\frac{d(\Delta G^{\circ})}{dT} \right)_p = \Delta G^{\circ} - RT^2 \left(\frac{d \ln K_p}{dT} \right) \rightarrow (4)$$

From Gibb's Helmholtz eqnⁿ

$$\Delta G^{\circ} = \Delta H^{\circ} + T \left[\frac{d(\Delta G^{\circ})}{dT} \right]_p \rightarrow (5)$$

$$T \left[\frac{d(\Delta G^{\circ})}{dT} \right]_p = \Delta H^{\circ} + T \left[\frac{d(\Delta G^{\circ})}{dT} \right]_p - RT^2 \left(\frac{d \ln K_p}{dT} \right)$$

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

$$\Rightarrow \frac{\Delta H^{\circ}}{RT^2} = \frac{d \ln K_p}{dT} \rightarrow (7)$$

Here ΔH° is the standard enthalpy of the reaction. This eqnⁿ (7) is known as Van't Hoff's equation.

Integrated form of Van't Hoff's equation:-

Integrated form of Van't Hoff's equation can be obtained by integrating equation (7).

(5)

$$\int \frac{d \ln K_p}{dT} = \int \frac{\Delta H^\circ}{RT^2}$$

$$\rightarrow \int d \ln K_p = \int \frac{\Delta H^\circ}{RT^2} dT \rightarrow (8)$$

If ΔH° depends upon temp^r over a very small range, then ΔH° is assumed to be temperature independent. Then equⁿ (8) can be written as,

$$\int d \ln K_p = \frac{\Delta H^\circ}{R} \int \frac{dT}{T^2} \rightarrow (9)$$

$$\ln K_p = \frac{-\Delta H^\circ}{RT} + I \rightarrow (10)$$

Where I is the integration constant.

If we integrate equⁿ (9) between two temp^s, T_1 and T_2 (with equi^m constants K_{p1} and K_{p2} respectively), then, assuming ΔH° is constant over this temperature range, we obtain

$$\int_{K_{p1}}^{K_{p2}} d \ln K_p = \frac{\Delta H^\circ}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{R} \left[-\frac{1}{T_2} - \left(-\frac{1}{T_1} \right) \right]$$

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

$$\ln \frac{K_{p2}}{K_{p1}} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \rightarrow (11)$$

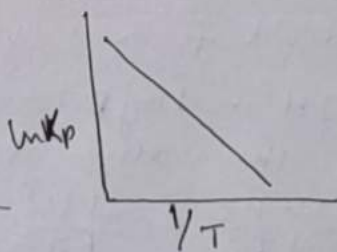
This equation is integrated van't Hoff equation.

(a) For endothermic reaction ($\Delta H = +ve$)

From equⁿ (10)

$$\ln K_p = \frac{-\Delta H^\circ}{RT} + I$$

On increasing temp^r K_p increases



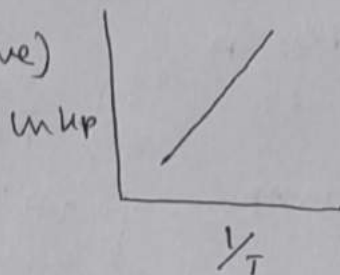
(6)

(b) For exothermic reaction ($\Delta H = -ve$)

$$\ln K_p = \frac{-\Delta H^0}{RT} + I$$

$$= -\left(\frac{-\Delta H^0}{RT}\right) + I$$

$$\ln K_p = \frac{\Delta H^0}{RT} + I$$



ie. On increasing temperature, K_p decreases.

values of ΔH^0 can be obtained by direct calorimetric measurement at constant pressure.

Van't Hoff equation in terms of K_c .

K_p is related to K_c according to the relation.

$$K_p = K_c (RT)^{\Delta n_g} \rightarrow \textcircled{1} \quad \Delta n_g = \left(\begin{array}{l} \text{no. of moles of product} \\ - \text{no. of moles of reactant} \end{array} \right)$$

Taking logarithm of both the sides,

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

Differentiating w.r.t. temperature, we get

$$\frac{d \ln K_p}{dT} = \frac{d \ln K_c}{dT} + \frac{\Delta n_g}{T} \rightarrow \textcircled{2}$$

But, we already have $\frac{d \ln K_p}{dT} = \frac{\Delta H^0}{RT^2} \rightarrow \textcircled{3}$

Combining eqnⁿ $\textcircled{1}$ & $\textcircled{2}$

$$\frac{d \ln K_c}{dT} + \frac{\Delta n_g}{T} = \frac{\Delta H^0}{RT^2}$$

$$\text{or } \frac{d \ln K_c}{dT} = \frac{\Delta H^0}{RT^2} - \frac{\Delta n_g}{T}$$

$$\text{or } \frac{d \ln K_c}{dT} = \frac{\Delta H^0 - \Delta n_g RT}{RT^2} \rightarrow \textcircled{4}$$

We know that $\Delta H = \Delta U + P\Delta V$.

In standard form $\Delta H^0 = \Delta U^0 + P\Delta V = \Delta U^0 + \Delta n_g RT$

$$\text{or } \Delta H^0 - \Delta n_g RT = \Delta U^0$$

Putting the value of ΔU^0 in eqnⁿ $\textcircled{4}$.

$$\frac{d \ln K_c}{dT} = \frac{\Delta U^0}{RT^2} \rightarrow \textcircled{5} \quad \left\{ \begin{array}{l} \text{It is the Van't Hoff eqn} \\ \text{in terms of } K_c \end{array} \right.$$