

Chemical Equilibrium

❖ Conditions For Thermodynamic Equilibrium:

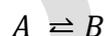
A system is said to be under thermodynamic equilibrium when it fulfill the following three main criteria—

- (i) Thermal equilibrium: The temperature at all parts of the system will remain fixed & unchanged.
- (ii) Chemical equilibrium: Chemical composition will remain fixed & unchanged, i.e. there will be no chemical reaction within the system.
- (iii) Mechanical equilibrium: There will be no unbalanced forced between the different parts of the system & also between the system & its adjacent surroundings.

❖ Extent of a Reaction:

Extent of a reaction is a quantity that measures the extent in which the reaction proceeds. It is usually denoted by ξ .

Consider the reaction,



Suppose an infinitesimal amount $d\xi$ of the reactant A changes into B. The change of the amount of A can be represented by the equation $dn_A = -d\xi$ & the change of B is $dn_B = +d\xi$.

The extent of the reaction is then defined as,

$$d\xi = \frac{dn_i}{v_i}$$

where n_i denotes the amount of the i – th reactant & v_i is the stoichiometric coefficient.

❖ Variation of Free Energy with ξ :

Variation of change in Gibbs reaction energy ($\Delta_r G$) with the extent of reaction or degree of advancement is given by the expression,

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T}$$

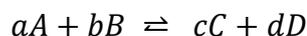
❖ Relation Between K_p , K_c & K_x :

Here, K_p = Equilibrium constant in terms of partial pressure.

K_c = Equilibrium constant in terms of partial concentration.

K_x = Equilibrium constant in terms of mole fraction.

Let us consider a general reaction,



Relation between K_p & K_c :

$$\text{We know, } K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

For n mole ideal gas,

$$PV = nRT, \text{ Or, } P = \left(\frac{n}{V}\right)RT = CRT$$

$$\begin{aligned} \text{Now, } K_p &= \frac{\left[\left(\frac{n_C}{V}\right)RT\right]^c \times \left[\left(\frac{n_D}{V}\right)RT\right]^d}{\left[\left(\frac{n_A}{V}\right)RT\right]^a \times \left[\left(\frac{n_B}{V}\right)RT\right]^b} \\ &= \frac{[C_C^c \times C_D^d]}{[C_A^a \times C_B^b]} \times (RT)^{(c+d)-(a+b)} \\ &= K_c \times (RT)^{\Delta n} \end{aligned}$$

where Δn = number of moles of product – number of moles of reactant.

Relation between K_p & K_x :

We know, Partial pressure = Total pressure \times Mole fraction. So,

$$P_A = P \times x_A$$

$$P_B = P \times x_B$$

$$P_C = P \times x_C$$

$$P_D = P \times x_D$$

$$\begin{aligned} \text{Now, } K_p &= \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b} \\ &= \frac{(x_C \cdot P)^c \times (x_D \cdot P)^d}{(x_A \cdot P)^a \times (x_B \cdot P)^b} \\ &= \frac{[x_C^c \times x_D^d]}{[x_A^a \times x_B^b]} \times (P)^{(c+d)-(a+b)} \\ &= K_x \times P^{\Delta n} \end{aligned}$$

➤ Derive the relation between K_p & K_c .

Follow above topic

➤ Derive the relation between K_c & K_x of a chemical reaction.

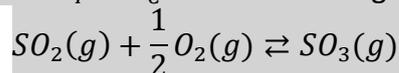
We know for n mole of ideal gas –

$$K_p = K_c \times (RT)^{\Delta n} \text{ \& } K_p = K_x \times P^{\Delta n}$$

So we can write,

$$\begin{aligned} K_c \times (RT)^{\Delta n} &= K_x \times P^{\Delta n} \\ \text{Or, } K_c &= K_x \left(\frac{P}{RT}\right)^{\Delta n} = K_x V^{-\Delta n} \end{aligned}$$

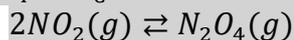
➤ Establish the relation between K_p & K_c for the following reaction:



$$\text{Here, } \Delta n = 1 - \left(1 + \frac{1}{2}\right) = -\frac{1}{2}$$

$$\begin{aligned} \text{We know, } K_p &= K_c \times (RT)^{\Delta n} \\ &= K_c \times (RT)^{-\frac{1}{2}} \end{aligned}$$

- Establish the relation between K_P & K_C for the following reaction:



$$\text{Here, } \Delta n = 1 - 2 = -1$$

$$\text{We know, } K_P = K_C \times (RT)^{\Delta n} \\ = K_C \times (RT)^{-1}$$

- Prove that for an ideal gas reaction –

$$\left(\frac{d \ln K_x}{dP} \right) = - \frac{\Delta n}{P}$$

$$\text{We know } K_P = K_x P^{\Delta n}$$

$$\text{Or, } K_x = K_P P^{-\Delta n}$$

$$\text{Or, } \ln K_x = \ln K_P - \Delta n \ln P$$

$$\text{Or, } \left(\frac{d \ln K_x}{dP} \right) = - \frac{\Delta n}{P} \text{ (proved)}$$

- For $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, by what factor would the value of K_P change if the standard state were taken to be 0.5 bar instead of 1 bar?

We can write –

$$K_P = \frac{(P_{NO_2}/P^0)^2}{\left(\frac{P_{N_2O_4}}{P^0} \right)} = \frac{P_{NO_2}^2}{P_{N_2O_4} P^0}$$

$$\frac{K_{P2}}{K_{P1}} = \frac{P_1^0}{P_2^0} = \frac{1}{1/2} = 2$$

$$\text{Or, } K_{P2} = 2K_{P1}$$

- Does the equilibrium constant of a chemical reaction depend on : (i) Standard state chosen for the reactants & products. & (ii) Stoichiometric representation of the reaction?

(i) Let for $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the standard state was taken to be 0.5 bar instead of 1 bar, then—

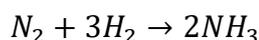
$$K_P = \frac{(P_{NO_2}/P^0)^2}{\left(\frac{P_{N_2O_4}}{P^0} \right)} = \frac{P_{NO_2}^2}{P_{N_2O_4} P^0}$$

$$\text{So, } \frac{K_{P2}}{K_{P1}} = \frac{P_1^0}{P_2^0} = \frac{1}{1/2} = 2$$

$$\text{Or, } K_{P2} = 2K_{P1}$$

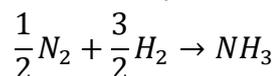
So, the equilibrium constant of a chemical reaction depend on Standard state chosen for the reactants & products.

(ii) Equilibrium constant of a reaction depends on the stoichiometry of the reaction. Equilibrium constant of a reaction can't be determined unless it is accompanied by a balanced chemical equation. For example—



$$\text{So, } K_{P1} = \frac{(P_{NH_3}/P^0)^2}{(P_{N_2}/P^0)(P_{H_2}/P^0)^3}$$

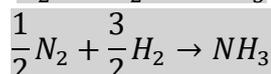
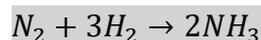
Now, dividing the both sides of the above equation by 2 –



$$\text{So, } K_{P_2} = \frac{(P_{NH_3}/P^0)}{(P_{N_2}/P^0)^{1/2}(P_{H_2}/P^0)^{3/2}}$$

Hence, $K_{P_1} \neq K_{P_2}$, ie, equilibrium constant of a reaction depends on the stoichiometry of the reaction.

- How are the k_p , at a particular temperature, for the following two cases related to each other?



For first reaction,

$$K_{P_1} = \frac{(P_{NH_3}/P^0)^2}{(P_{N_2}/P^0)(P_{H_2}/P^0)^3}$$

For 2nd reaction,

$$K_{P_2} = \frac{(P_{NH_3}/P^0)}{(P_{N_2}/P^0)^{1/2}(P_{H_2}/P^0)^{3/2}}$$

$$\text{Or, } (K_{P_2})^2 = \frac{(P_{NH_3}/P^0)^2}{(P_{N_2}/P^0)(P_{H_2}/P^0)^3} = K_{P_1}$$

Hence, $K_{P_1} = (K_{P_2})^2$.

- K_p is always dimensionless, is a function of temperature but is independent of pressure for a ideal gas reaction equilibrium – explain.

Since in the expression of K_p , each term is ratio of two pressure, so it is dimensionless.

K_p is a function of temperature because in an exothermic reaction with increase of temperature equilibrium will be shifted to backward direction whereas in endothermic reaction equilibrium will be shifted to forward direction.

But pressure only effects the equilibrium conditions and not the value of K_p because partial pressures are so adjusted to provide the same value of K_p at the same temperature. So, K_p is independent of P for a ideal gas reaction equilibrium.

❖ Chemical Potential of an Ideal Gas:

We know,

$$dG = VdP - SdT = VdP \text{ (at constant } T)$$

$$\text{Or, } \Delta G = G_2 - G_1 = \int_1^2 VdP$$

Applying this for n mole of ideal gas ($PV = nRT$), we get –

$$G_2 - G_1 = nRT \ln \frac{P_2}{P_1}$$

$$\text{Or, } \mu_2 - \mu_1 = RT \ln \frac{P_2}{P_1}$$

If we now choose our standard state as the gas 1 atmosphere ($\mu_1 = \mu^0$ at $P_1 = 1 \text{ atm}$), we get,

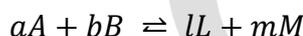
$$\mu_2 = \mu^0 + RT \ln \left(\frac{P_2}{1} \right)$$

In general we can write,

$$\mu_i = \mu_i^0 + RT \ln \left(\frac{P_i}{P^0} \right)$$

❖ Van't Hoff Reaction Isotherm:

Let us consider a general reaction,



where all the gases are ideal & kept at temperature T & pressure P.

$$\text{Now, } \Delta G = \sum G_{\text{product}} - \sum G_{\text{reactant}}$$

$$\text{Or, } \Delta G_{P,T} = (l\mu_L + m\mu_M) - (a\mu_A + b\mu_B)$$

$$\text{Now, substituting } \mu_i = \mu_i^0 + RT \ln \left(\frac{P_i}{P^0} \right)$$

$$\Delta G_{P,T} = \left[l \left(\mu_L^0 + RT \ln \frac{P_L}{P^0} \right) + m \left(\mu_M^0 + RT \ln \frac{P_M}{P^0} \right) \right] - \left[a \left(\mu_A^0 + RT \ln \frac{P_A}{P^0} \right) + b \left(\mu_B^0 + RT \ln \frac{P_B}{P^0} \right) \right]$$

$$= [(l\mu_L^0 + m\mu_M^0) - (a\mu_A^0 + b\mu_B^0)] + RT \ln \left[\frac{\left(\frac{P_L}{P^0} \right)^l \times \left(\frac{P_M}{P^0} \right)^m}{\left(\frac{P_A}{P^0} \right)^a \times \left(\frac{P_B}{P^0} \right)^b} \right]$$

$$= \Delta G_{T,P}^0 + RT \ln \left[\frac{\left(\frac{P_L}{P^0} \right)^l \times \left(\frac{P_M}{P^0} \right)^m}{\left(\frac{P_A}{P^0} \right)^a \times \left(\frac{P_B}{P^0} \right)^b} \right]$$

$$\text{Or, } \Delta G_{P,T} = \Delta G_{T,P}^0 + RT \ln Q_P$$

$$\text{where } Q_P = \left[\frac{\left(\frac{P_L}{P^0} \right)^l \times \left(\frac{P_M}{P^0} \right)^m}{\left(\frac{P_A}{P^0} \right)^a \times \left(\frac{P_B}{P^0} \right)^b} \right] \text{ is pressure quotient of the reaction.}$$

The above equation is known as van't Hoff reaction isotherm.

Under equilibrium condition, $\Delta G_{P,T} = 0$, so,

$$\Delta G_{T,P}^0 + RT \ln [Q_P]_{\text{equilibrium}}$$

$$\text{Or, } \Delta G_{T,P}^0 = -RT \ln [Q_P]_{\text{equilibrium}} = -RT \ln K_P$$

❖ Van't Hoff Equation in terms of K_p :

$$\Delta G^0 = -RT \ln K_p$$

$$\text{So, } \ln K_p = -\left(\frac{\Delta G^0}{RT}\right) = -\left(\frac{1}{R}\right)\left(\frac{\Delta G^0}{T}\right)$$

$$\text{Or, } \frac{d}{dT}(\ln K_p) = -\left(\frac{1}{R}\right)\left[\frac{d}{dT}\left(\frac{\Delta G^0}{T}\right)\right]$$

According to Gibb's – Helmholtz equation –

$$\left[\frac{d}{dT}\left(\frac{\Delta G^0}{T}\right)\right] = -\frac{\Delta H^0}{T^2}$$

$$\text{So, } \frac{d}{dT}(\ln K_p) = -\left(-\frac{\Delta H^0}{RT^2}\right) = \left(\frac{\Delta H^0}{RT^2}\right)$$

$$\text{Or, } \frac{d \ln K_p}{d\left(\frac{1}{T}\right)} = -\left(\frac{\Delta H^0}{R}\right)$$

Here ΔH^0 is standard enthalpy change of the reaction.

Assumption: Here ΔH^0 is assumed to be independent of given temperature limit T_1 & T_2 .

Integrated form:

$$\int_1^2 d \ln K_p = \frac{\Delta H^0}{R} \int_1^2 \frac{dT}{T^2}$$

$$\begin{aligned} \text{Or, } \ln \left(\frac{K_{p_2}}{K_{p_1}}\right) &= \frac{\Delta H^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ &= \frac{\Delta H^0}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \end{aligned}$$

i. For endothermic reaction, $\Delta H = +ve$, then –

$$\ln \left(\frac{K_{p_2}}{K_{p_1}}\right) = +ve, \text{ so, } K_{p_2} > K_{p_1}$$

It means that equilibrium constant increases with increase in temperature.

ii. For exothermic reaction, $\Delta H = -ve$, then –

$$\ln \left(\frac{K_{p_2}}{K_{p_1}}\right) = -ve, \text{ so, } K_{p_2} < K_{p_1}$$

It means that equilibrium constant decreases with increase in temperature.

❖ Van't Hoff Equation in terms of K_C :

We know, $K_P = K_C(RT)^{\Delta n}$

$$\text{So, } \ln K_P = \ln K_C + \Delta n \ln R + \Delta n \ln T$$

$$\text{Or, } \frac{d \ln K_P}{dT} = \frac{d \ln K_C}{dT} + \frac{\Delta n}{T}$$

$$\text{Or, } \left(\frac{\Delta H}{RT^2} \right) = \frac{d \ln K_C}{dT} + \frac{\Delta n}{T}$$

$$\text{Or, } \frac{d \ln K_C}{dT} = \left(\frac{\Delta H}{RT^2} \right) - \frac{\Delta n}{T}$$

We know, $\Delta H = \Delta U + \Delta nRT$

$$\text{So, } \Delta U = \Delta H - \Delta nRT$$

Comparing these two equations,

$$\frac{d \ln K_C}{dT} = \frac{\Delta H - \Delta nRT}{RT^2} = \frac{\Delta U}{RT^2}$$

For standard state,

$$\frac{d \ln K_C}{dT} = \frac{\Delta U^0}{RT^2}$$

Assumption: Here ΔU^0 is assumed to be independent of given temperature limit T_1 & T_2 .

Integrated form:

$$\int_1^2 d \ln K_C = \frac{\Delta U^0}{R} \int_1^2 \frac{dT}{T^2}$$

$$\begin{aligned} \text{Or, } \ln \left(\frac{K_{C_2}}{K_{C_1}} \right) &= \frac{\Delta U^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{\Delta U^0}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \end{aligned}$$

➤ Write the vant Hoff's equation related to chemical equilibrium & temperature.

$$\frac{d \ln K_P}{dT} = \left(\frac{\Delta H^0}{RT^2} \right)$$

Here ΔH^0 is standard enthalpy change of the reaction.

VJRC