

Chemical Equilibrium



By
Nitesh Jain (B.tech, IIT Bombay)

Chemical Equilibrium and Equilibrium Constant

For a general reaction: $aA + bB \rightleftharpoons cC + dD$

NOTE: Reactions are generally reversible i.e. can proceed both ways

A reaction attains equilibrium when

rate of forward reaction (r_f) = rate of backward reaction (r_b)

From Law of Mass Action

$$r_f = k_f[A]^a[B]^b$$

$$r_b = k_b[C]^c[D]^d$$

[] represents concentration

k_f and k_b are rate constants of forward and backward reactions respectively

$k_f[A]^a[B]^b = k_b[C]^c[D]^d$ are rate constants of forward and backward reactions respectively

$$\frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

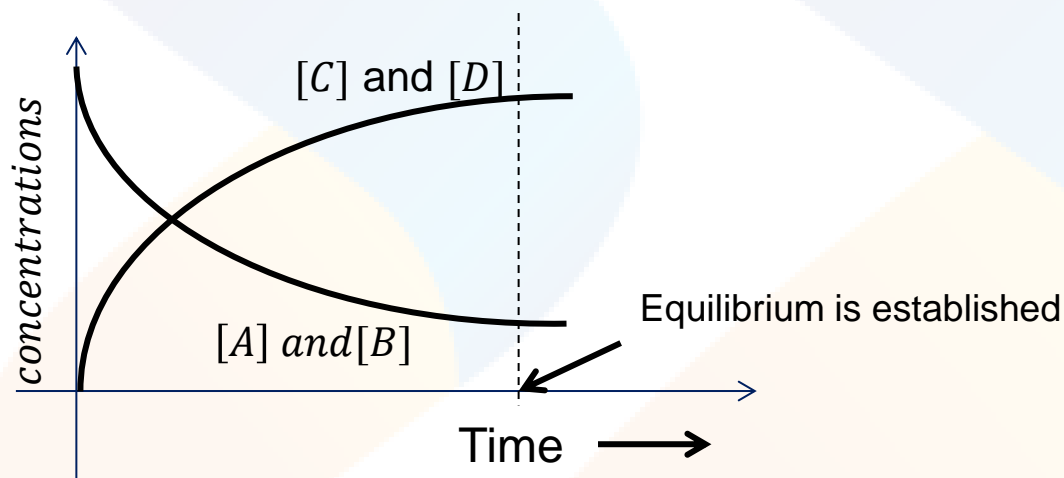


$$\frac{k_f}{k_b} = K(\text{equilibrium constant})$$

Dynamic Nature of Chemical Equilibrium

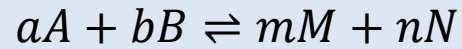
For reaction: $aA + bB \rightleftharpoons cC + dD$

(equilibrium constant) $K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ \longrightarrow K in terms of concentration is called K_c



NOTE: Chemical equilibrium is dynamic as, individual molecules are continually reacting, even though overall composition of reaction mixture doesn't change

Homogenous Gaseous Reaction



All A, B, M and N are gases

Let p_x represent partial pressure of specie x at equilibrium

$$p_x = \frac{n_x}{n_{total}} \times P$$

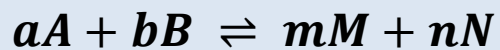
P = total Pressure
 n_{total} = total #of moles

then

$$K_p = \frac{p_M^m p_N^n}{p_A^a p_B^b}$$

Here, K_p is known as pressure equilibrium constant

Relation between K_p and K_c



K_c can also be written for the reaction, but for the above reaction calculating. K_p is easier



$$K_p = K_c(R.T)^{\Delta n}$$

$\Delta n = \text{no. of moles of product} - \text{no. of moles of reactant}$

Example: $\Delta n = (m + n) - (a + b)$, for above reaction



Stoichiometric coefficients after balancing reaction

Equilibrium constant depend only on temperature

Both K_p and K_c given same information about the state of equilibrium

Units of K_p and K_c are not fixed and depend on stoichiometry of the reaction

Mole Fraction Equilibrium Constant (K_x)

for a reaction: $aA + bB \rightleftharpoons mM + nN$

Mole fraction of specie $Z = \frac{n_z(\text{number of moles of } Z)}{n_{\text{total}}(\text{total number of moles})} = x_z(\text{dimensionless})$

$$K_x = \frac{x_M^m x_N^n}{x_A^a x_B^b}$$

K_x does not have any unit

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

$\Delta n = \text{no. of moles of product} - \text{no. of moles of reactant}$

NOTE: $K_p = K_c = K_x$, for $\Delta n = 0$

K_x may depend on P or V , unlike K_p and K_c

Thermodynamic Definition of Equilibrium Constant

It involves activities of reactants and products, rather than their concentration, by definition



∴ Thermodynamic **equilibrium constant has no unit**

NOTE: For any pure solid or pure liquid, **activity= 1**

Activity of a component (X)

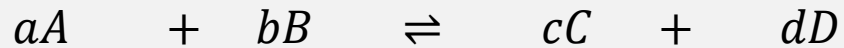
$$\frac{[X] \text{ (concentration of } X\text{)}}{1M}$$

$$\frac{p_x \text{ (partial pressure of } X\text{)}}{1 \text{ atm}}$$

NOTE: It is a dimensionless quantity

Calculation of Degree of Dissociation

Consider a reaction: in a container of **Volume V**



initially a_0 b_0 0 0

At equilibrium $a_0(1 - \alpha)$ $b_0(1 - \alpha)$ $c\alpha$ $d\alpha$

α is always less than 1
for equilibrium reactions

α is called degree of dissociation, which is defined per mole of **limiting reactant**
(assumed A in example)

$$\begin{aligned}\text{Total number of moles at equilibrium} &= c\alpha + d\alpha + (a_0 - a_0\alpha) + (b_0 - b_0\alpha) \\ &= (a_0 + b_0) + \alpha(c + d - a - b) \\ &= (a_0 + b_0) + \alpha(\Delta n)\end{aligned}$$



This expression derived for a general reaction would be helpful in **calculating α or k**

Degree of Dissociation from Density

If one mole of substance dissociates into n moles, into container of Volume V

Reaction:	A	\rightleftharpoons	$n.B$	
Initially moles	1		0	$\longrightarrow d_t \propto \frac{1}{V}$
At equilibrium	$(1 - x)$		$n.x$	$\longrightarrow d_0 \propto \frac{1}{V[1 + (n - 1)x]}$

NOTE: The equation is not applicable to reactants in which
of moles of reactants = # moles of products

$$\text{Degree of dissociation } x = \frac{d_t - d_0}{(n - 1)d_0}$$

Both under same pressure

d_t = theoretical density (assuming no dissociation)
 d_0 = observed/ experimental density

$$x = \frac{M - m}{(n - 1)m}$$

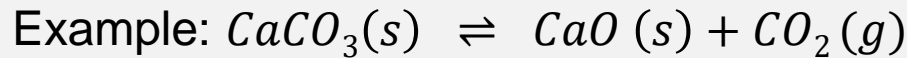
M Initial molecular mass
 m --Molecular mass of equilibrium

NOTE: If all d 's are taken as vapor densities,

$$d_t = \frac{\text{molecular weight}}{2}$$

Pure Solids Involved in Chemical Reaction

Concentrations of pure solids involved in a chemical reaction, are assumed to remain constant



$$K = \frac{[\text{CaO}][\text{CO}_2]}{[\text{CaCO}_3]}$$



$[\text{CaO}] \rightarrow \text{Constant } [x_1]$

$[\text{CaCO}_3] \rightarrow \text{Constant } [x_2]$

$$K = \frac{x_1[\text{CO}_2]}{x_2}$$



$$K' = [\text{CO}_2]$$



NOTE: $K' = K \left(\frac{x_2}{x_1} \right)$ becomes the equilibrium constant of the reaction

Relation Between Equilibrium Constants of Forward & Backward Reactions

For a reaction: $aA + bB \rightleftharpoons cC + dD$

At equilibrium : Forward Reaction $\longrightarrow aA + bB \rightarrow cC + dD$

$$K_f = \frac{[C]^c [D]^d}{[A]^a [B]^b} \longrightarrow 1$$

For Backward Reaction: $\longrightarrow cC + dD \rightarrow aA + bB$

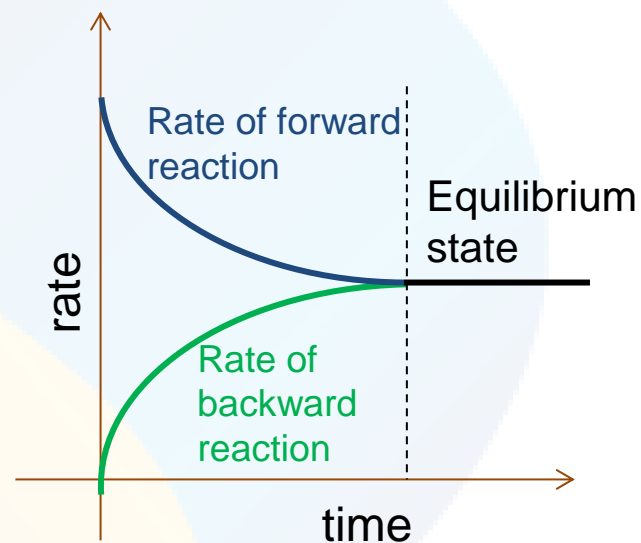
$$K_b = \frac{[A]^a [B]^b}{[C]^c [D]^d} \longrightarrow 2$$

From 1 and 2

$$K_f \cdot K_b = 1$$

$$\longrightarrow K_f = \frac{1}{K_b}$$

i.e. K_f and K_b are reciprocal of each other

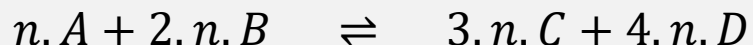


Multiplication of Chemical Equation by Certain Factor

Consider a reaction: $A + 2B \rightleftharpoons 3C + 4D$

$$K = \frac{[C]^3[D]^4}{[A]^1[B]^2}$$

Multiplying the chemical equation by a factor n



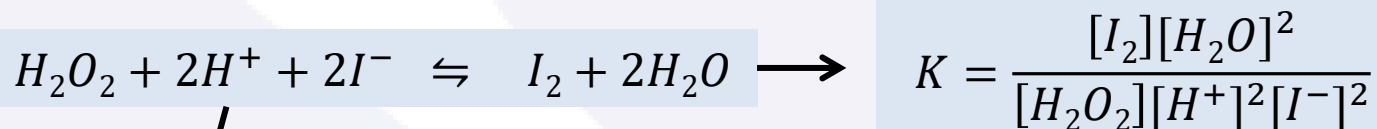
$$K' = \frac{[C]^{3n}[D]^{4n}}{[A]^n.[B]^{2n}} = (K)^n$$

$$K' = K^n$$

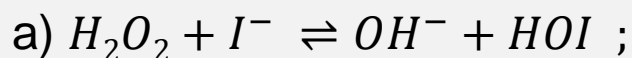
New equilibrium constant will be old equilibrium constant raised to a power equal to the multiplies factor

Reactions Taking Place in more than One Step

Example: For reaction



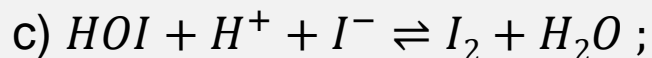
This reaction takes place in steps as:



$$K_1 = \frac{[OH^-][HOI]}{[H_2O_2][I^-]}$$



$$K_2 = \frac{[H_2O]}{[H^+][OH^-]}$$



$$K_3 = \frac{[H_2O][I_2]}{[HOI][H^+][I^-]}$$

$$K_1 \cdot K_2 \cdot K_3 = K$$

Equilibrium constant of overall reaction is equal to the product of equilibrium constant of each other step

Reaction Quotient (Q)

For a reaction: $aA + bB \rightleftharpoons mM + nN$

$$Q = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

→ Not necessarily equilibrium concentration

Q tells → Whether the reaction is at equilibrium or not

→ Direction of reaction when equilibrium constant of reaction is known

Equilibrium concentrations

$$K = \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

1

$Q > K$: Reaction proceeds in backward direction

2

$Q = K$: Reaction is at equilibrium

3

$Q < K$: Reaction proceeds in Forward Direction

Le Chatelier's Principle

Effect of change on a reaction at equilibrium, shifts the reaction in a direction that minimizes that change

These changes can be change in temperature, pressure or concentration



These changes cannot change the equilibrium constant K_p or K_c , except change in temperature

Effects of Temperature on Equilibrium Constant

Van't Hoff equation:

$$\log K_{p2} - \log K_{p1} = \frac{\Delta H^\circ}{2.303 \cdot R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right], T_2 > T_1$$

- ✓ K_{p1} and K_{p2} are equilibrium constants at temperatures T_1 and T_2 respectively
- ✓ ΔH° is standard heat of reaction at constant pressure [assumed constant for small $(T_2 - T_1)$]

NOTE: No shift in equilibrium for $\Delta H = 0$

$K_{p2} > K_{p1}$, if ΔH° is **positive** → endothermic reaction

$K_{p2} < K_{p1}$, if ΔH° is **negative** → exothermic reaction

For an exothermic reaction, increase in temperature results in shifting reaction towards endothermic path i.e. from right to left or towards reactants AND vice-versa for endothermic reaction

Le Chatelier's Principle: Effect of Pressure

At constant T, V of reaction \longrightarrow No. of moles \propto Pressure

1

For a reaction : $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

$P_x =$ partial pressure of x

$$= \frac{n_C^c n_D^d}{n_A^a n_B^b} \times \left(\frac{P}{n_{total}} \right)^{\Delta n}$$

From 1, where
 $n_x =$ # moles of X at equilibrium

$$\Delta n = (c + d) - (a + b)$$

And from above, $K_p \propto (P)^{\Delta n}$

NOTE: $\Delta n = 0 \Rightarrow$ equilibrium is not affected

If P is increased \longrightarrow

$\Delta n = +ve \Rightarrow$ equilibrium shifts **towards left** (to increase $a + b$)

$\Delta n = -ve \Rightarrow$ equilibrium shifts **towards right** (to increase $c + d$)

Le Chatelier's Principle: Effect of Addition of Inert Gas

CASE 1: At constant Volume

Equilibrium is **not affected at all**

CASE 2: At constant Pressure

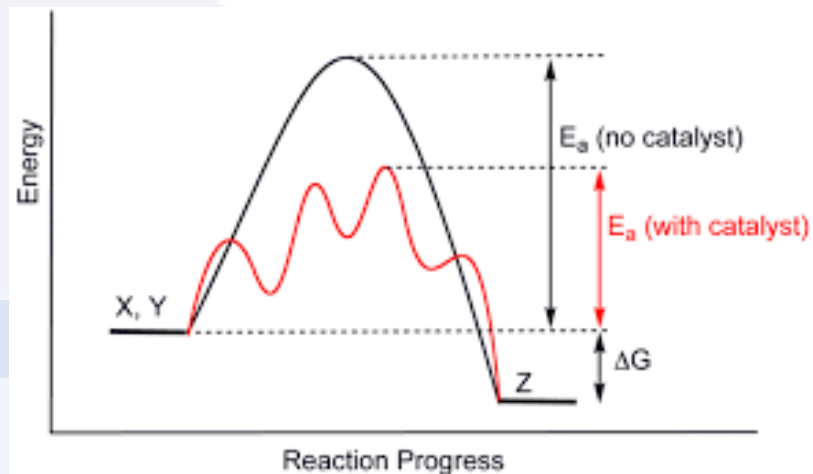
a) $\Delta n = 0 \Rightarrow$ *equilibrium is not affected*

b) $\Delta n = +ve \Rightarrow$ *equilibrium is **shifted to the right** (towards products)*

c) $\Delta n = -ve \Rightarrow$ *equilibrium is **shifted to left** (towards reactants)*

Le Chatelier's Principle: Effect of Addition of Catalyst

Addition of catalyst changes the rate of reaction



Catalyst affects the activation energy (E_A) of both forward and backward reactions equally

If K_f and K_b are rate constants of forward and backward reactions respectively

$$K_c = \frac{K_f}{K_b} = \frac{K_{f'}}{K_{b'}}$$

Both rate constants are affected equally

NOTE: Both reaction Quotient Q and K are not affected due to addition of catalyst.

But time requires to establish equilibrium is altered

Le Chatelier's Principle: Effect of removal/addition of Reactants/Products

On addition or removal of reactants/products at equilibrium



Equilibrium shifts in direction that consumes or produces that reactant(s)/product(s)



NOTE: This is valid only if volume of system is kept constant

If volume of system is not constant but at constant pressure

→ *direction of shifting of equilibrium depends on Δn*

Relation between Free Energy Change and K

$$\Delta G = \Delta G^\circ + R.T.\ln Q$$

1

ΔG° is standard free energy change for a reaction and ΔG is free energy change

Standard conditions imply 1M or 1 atm of reactants converting to 1M or 1 atm of products

At equilibrium, $\Delta G = 0$ and $Q = K$

\therefore From 1

$$\Rightarrow \Delta G^\circ = -R.T.\ln K$$

$$= -2.303 R.T.\log K$$

NOTE: In case all gaseous reactants & products

$$K = K_p$$

In case of all solution reactants & products,

$$K = K_c$$

In case of mixture of solution & gaseous reactants and products, K represents thermodynamic equilibrium constant

Feasibility of Reaction from Free Energy Change

$$\Delta G^\circ = -R.T.\ln K$$



1 $\Delta G^\circ < 0 \Rightarrow K > 1$ *i.e. a forward reaction is feasible*

2 $\Delta G^\circ = 0$ or $K = 1$ *i.e. reaction is at equilibrium*

3 $\Delta G^\circ > 0 \Rightarrow K < 1$ *i.e. a reverse reaction is feasible*

NOTE: For a spontaneous or feasible reaction $\Delta G^\circ < 0$

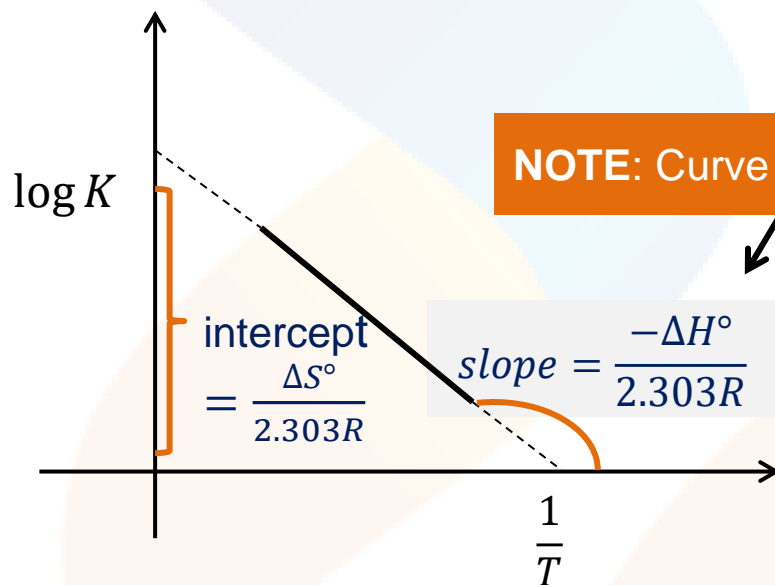
Calculation of ΔG° and ΔS° from K

From Thermodynamics: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ \longrightarrow 1

$$\Delta G^\circ = -R \cdot T \cdot \ln K \longrightarrow 2$$

From 1 and 2

$$\log K = \frac{-\Delta H^\circ}{2.303R} \cdot \frac{1}{T} + \frac{\Delta S^\circ}{2.303R}$$

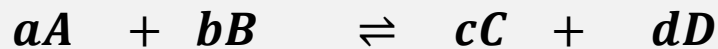


NOTE: Curve between $\log K$ and $\log \frac{1}{T}$ gives a straight line

Knowing ΔH° and ΔS° , ΔG° can be calculated from 1

Calculation K_p and K_c

Consider a reaction: in a container of *Volume V*



initially a_0 b_0 0 0

At equilibrium $a_0(1 - \alpha)$ $b_0(1 - \alpha)$ $c\alpha$ $d\alpha$ \longrightarrow

α is degree of dissociation
w.r.t limiting reagent A

$$K_c = \frac{[C]_{equi}^c [D]_{equi}^d}{[A]_{equi}^a \cdot [B]_{equi}^b}$$

$$K = \frac{\left(\frac{C\alpha}{V}\right)^c \cdot \left(\frac{d\alpha}{V}\right)^d}{\left(\frac{a_0 - a_0\alpha}{V}\right)^a \cdot \left(\frac{b_0 - b_0\alpha}{V}\right)^b}$$

General expression and can be used
directly for finding out K_c

$$= \left(\frac{C^c \cdot d^d}{a_0^a \cdot b_0^b}\right) \times \frac{\alpha^{c+d}}{(1 - \alpha)^{a+b}} \times \frac{1}{V^{\Delta n}}$$

\longrightarrow Where $\Delta n = (c + d) - (a + b)$

NOTE: $K_p = K_c(R.T)^{\Delta n}$, K_p can also be calculated, if α is known