MIND MAP

FOR NEET ASPIRANTS

PHYSICAL CHEMISTRY

CHEMICAL EQUILIBRIUM

ONE-SHOT

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Topics *to be covered*

min 2Q

1. Equilibrium → Introduction
2. Physical Equilibrium
3. Equilibrium Constant and its applications
4. le-chattelier's principle

Introduction

Equilibrium → stage of rxn where net rate of reactions becomes zero because rate of forward rxn = rate of Backward rxn.

- Overall rxn seems to be stopped but at molecular level, rxn occurs in both directions at same speed.
- values of all measurable properties become constant.
  - K_{eq} → equilibrium constant
- → is possible only for Reversible rxn ($R \rightleftharpoons P$)
- → is possible in closed vessel.
- Dynamic in nature

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

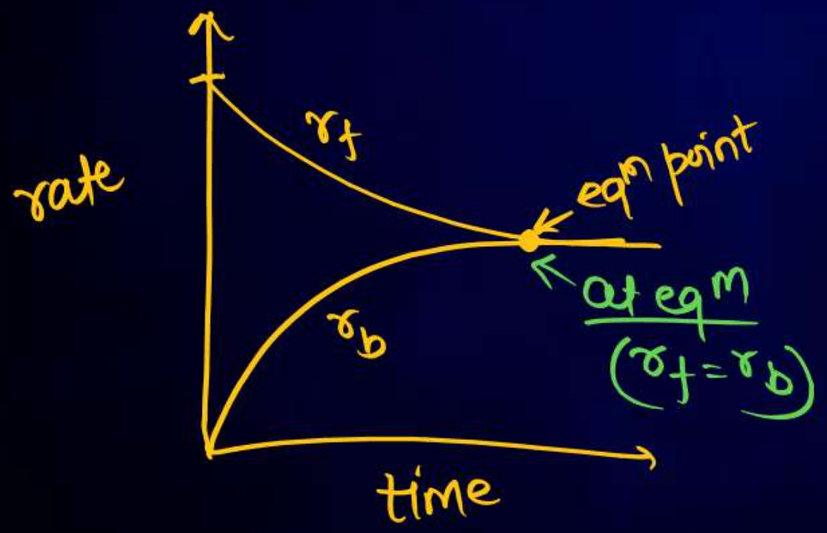
(Open vessel) ✗

(Closed vessel) ✓

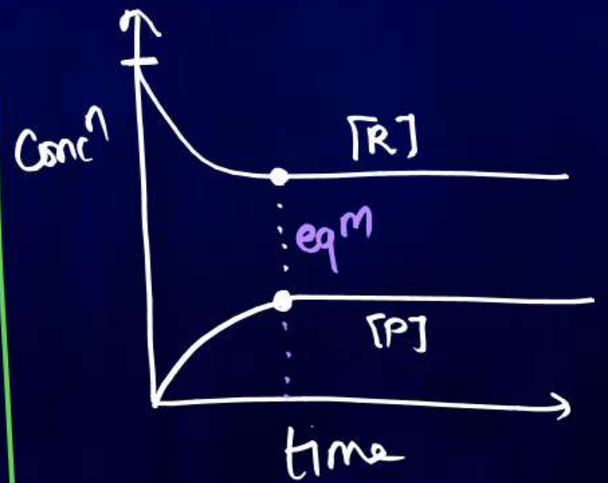
Graphs of Equilibrium

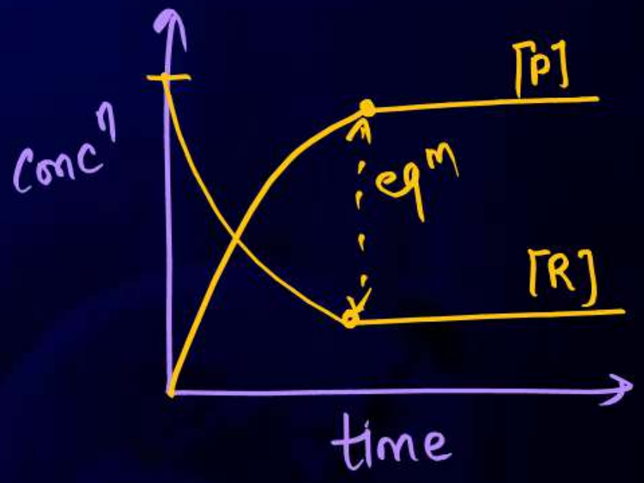
eqn = equation
eqm = equilibrium

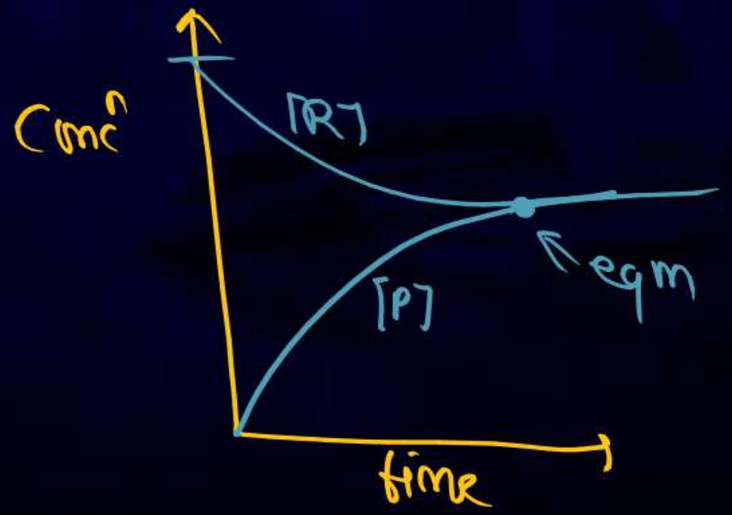
① rate Vs time



② Concn Vs time







Equilibrium stage → Balance of driving force → max. stability or minimum energy ($\Delta H<0$)

→ max. randomness ($\Delta S>0$)

→ $(\text{rate})_{\text{forward}} = (\text{rate})_{\text{Backward}}$.

→ equilibrium mixture contains reactant as well as product.

→ dynamic in nature

Equilibrium

↓ on the basis of phases of reactants and products

→ Homogeneous Eqm ⇒ only one phase of reactants and products are present

$$\left\{ \begin{matrix} R_{(s)} \rightleftharpoons P_{(s)} \\ R_{(g)} \rightleftharpoons P_{(g)} \end{matrix} \right\}$$

→ Hetrogeneous Eqm ⇒ more than one phase of reactants and products are present.

$$\begin{matrix} R_{(s)} \rightleftharpoons P_{(g)} \\ R_{(g)} \rightleftharpoons P_{(s)} \end{matrix}$$

Equilibrium → on the basis of processes involved

physical eqm

eqm involving physical changes.

$$A_{(s)} \rightleftharpoons A_{(l)}$$
$$A_{(s)} \rightleftharpoons A_{(g)}$$

Chemical eqm

eqm involving chemical rxn

$$H_2 + Cl_2 \rightleftharpoons 2HCl$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Ionic Eqm

eqm involving ions in the rxn.

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$
$$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$

Physical Eqm → for Reversible process in a closed container } only physical changes

① Solid-liquid Eqm

$A(s) \rightleftharpoons A(\ell)$

at eqm ⇒ rate of fusion of A(s) = rate of crystallisation of A(ℓ)

Temp = M.pt or f.pt

② Liquid-Gas Eqm

$A(\ell) \rightleftharpoons A(g)$

at eqm ⇒ rate of vaporisation of A(ℓ) = rate of condensation of A(g)

Temp = B.pt

③ Solid-Gas eqm

$A(s) \rightleftharpoons A(g)$

at eqm ⇒ rate of sublimation of A(s) = rate of de-sublimation of A(g)

④ Eqm in Dissolution of solid in liquid

Solid (solute) + liquid (solvent) $\rightleftharpoons$ Solution

At eqm, rate of dissolution of solid in liquid = rate of crystallization of solid from solution.

⑤ Eqm in dissolution of Gas in liquid

Gas (solute) + liquid (solvent) $\rightleftharpoons$ Solution → always exothermic

At eqm → rate of dissolution of gas in liquid = rate of escape of gas from liquid.

Solubility of gas in liquid $\propto \frac{1}{\text{Temp}}$

$\propto$ Pressure → Henry's law

Active Mass ⇒ for gases, active mass = Pressure

→ for liquid solution, active mass = Concentration / Molarity (n/v)

→ for solids and pure liquids, active mass = 1

→ intensive property as Molecular mass and density always constant

Concentration is represented by [ ]

[A] = Conc^n of A

Law of mass action

$$aA + bB \rightleftharpoons cC + dD$$

a, b, c, d → Stoichiometric coefficient

$$(\text{rate})_{\text{forward}} \propto [A]^a [B]^b$$

$$(\text{rate})_f = k_f [A]^a [B]^b$$

k_f → rate constant for forward rxn

$$(\text{rate})_{\text{Backward}} \propto [C]^c [D]^d$$

$$(\text{rate})_B = k_b [C]^c [D]^d$$

k_b → rate constant for Backward rxn

Rate of rxn $\propto$ [Reactant]^n

$\text{Rate} = k [R]^n$

k → rate constant

Law of chemical equilibrium

At eqm → Net rate of rxn = 0

$(\text{rate})_f - (\text{rate})_b = 0$

$(\text{rate})_f = (\text{rate})_b$

$k_f [A]^a [B]^b = k_b [C]^c [D]^d$

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

k_f → rate Constant for forward rxn

k_b → rate Constant for Backward rxn

$$aA + bB \rightleftharpoons cC + dD$$

In terms of Concentration

$$(K_{eq})_{Conc^n} = K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

In terms of Pressure

$$(K_{eq})_{Pressure} = K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

In terms of mole fraction

$$(K_{eq})_{mole\ fraction} = K_x = \frac{(x_C)^c (x_D)^d}{(x_A)^a (x_B)^b}$$

Factors affecting K_{eq}

① Temp:

$$\ln K_{eq} = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

→ for endothermic rxn, $K_{eq} \propto$ Temp.

→ for exothermic rxn, $K_{eq} \propto \frac{1}{\text{Temp}}$

$$\Delta G^\circ = -RT \ln K_{eq} = \Delta H^\circ - T\Delta S^\circ$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

② Stoichiometry of rxn

$A \rightleftharpoons B$ $\quad K_{eq} = K_1$

multiplied by (n), $nA \rightleftharpoons nB$ $\quad K_{eq} = (K_1)^n$

divided by (m) or multiplied by $\left(\frac{1}{m}\right)$, $\frac{1}{m}A \rightleftharpoons \frac{1}{m}B$ $\quad K_{eq} = (K_1)^{\frac{1}{m}}$

③ Mode of Representation of rxn

$A \rightleftharpoons B \quad K_{eq} = K_1 = \frac{[B]}{[A]}$

On reversing the rxn

$B \rightleftharpoons A \quad K_{eq} = \frac{1}{K_1} = \frac{[A]}{[B]}$

$(K_{eq})_{forward} \propto (K_{eq})_{Backward} = 1$

④ Multi-step rxn

$A \rightleftharpoons \cancel{B} \quad K_{eq} = K_1$

$\cancel{B} \rightleftharpoons C \quad K_{eq} = K_2$

$A \rightleftharpoons C \quad K_{eq} = K_1 \times K_2$

Keq does not depends on

1. Concentration of Reactant and Products.
2. Pressure
3. Catalyst
4. Volume
5. Steps of rxn
6. Insertion of inert material

Relation b/w K_p K_c and K_x

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

- $\Delta ng > 0$ → $K_p > K_c$
- $\Delta ng < 0$ → $K_p < K_c$
- $\Delta ng = 0$ → $K_p = K_c$

$RT = 1$ → $K_p = K_c$

$T = \frac{1}{R} \simeq 12K$

$$K_p = K_x (P_{total})^{\Delta ng}$$

- if $\Delta ng = 0$ → $K_p = K_x$
- if $P_{total} = 1$ → $K_p = K_x$

For any rxn

Δng = no. of gaseous moles of product - reactant

$\Delta ng = 0$ → $K_p = K_c = K_x$

Units of K_{eq}

1. Unit of K_x = unitless
2. Unit of K_c = (unit of conc^n)$^{\Delta n}$ → where Δn = no. of moles of product - reactant.
3. Unit of K_p = (unit of pressure)$^{\Delta ng}$ → where Δng = no. of gaseous moles of product - reactant.

Application of K_{eq}

① Extent of rxn

$$K_{eq} = \frac{[P]}{[R]}$$

- $K_{eq} > 10^3$ or 1000
  - → equilibrium mixture have mostly products.
  - → [Products] >>> [Reactants]
  - → Product is more stable than reactant.
  - → rxn is almost at Completion.
- $K_{eq} < 10^{-3}$ or $\frac{1}{1000}$
  - → eqm mixture have mostly reactants.
  - → [Reactants] >>> [Products.
  - → Reactant is more stable than Products.
  - → rxn just started.
- $10^{-3} < K_{eq} < 10^3$ → eqm mixture have significant amount of products as well as reactants.

② Direction of Rxn

Q_c, Q_p

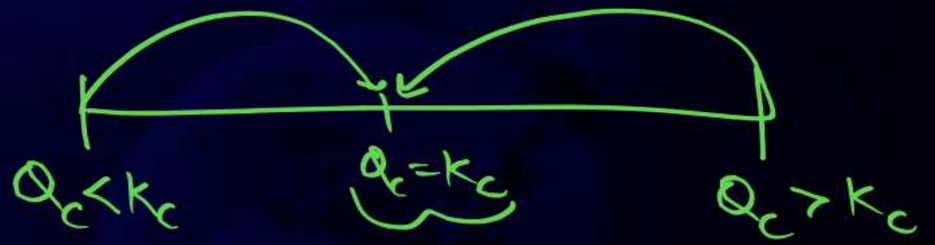
Q = Reaction Quotient

- same expression as K_{eq}.
- defined at any moment of rxn.
- value of Q varies during the rxn.
- depends on Temp as well as Conc^n, pressure, volume.

$Q_c > K_c \Rightarrow$ eqm will shift in backward direction.

$Q_c = K_c \rightarrow$ at equilibrium.

$Q_c < K_c \rightarrow$ eqm will shift in forward direction.



$\Delta G^\circ = -RT \ln K_{eq}$

$= -2.303\, RT \log K_{eq}$

$\Delta G = \Delta G^\circ + RT \ln Q_c$

at eqm $\Rightarrow \Delta G = 0$

Spontaneous process, $\Delta G < 0$

$K_{eq} > 1$

$\Delta S_{total} > 0$

Non-spontaneous rxn: $\Delta G > 0$, $K_{eq} < 1$, $\Delta S_{total} < 0$

Calculation of Equilibrium Mixture

Case-I → if initial conc^n & K_c is given

$$A \rightleftharpoons B + C$$

	A	B	C
t=0	C	0	0
t=eqm	C-x	x	x

$$K_{eq} = K_c = \frac{[B][C]}{[A]}$$

$$K_c = \frac{x \cdot x}{C-x}$$

at eqm

$[A] = C-x$

$[B] = x$

$[C] = x$

Case-II → if initial Pressure and K_p is given

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$$

	A	B	C
t=0	P_0	0	0
t=eqm	P_0-x	x	x

$$K_p = \frac{(P_B)(P_C)}{(P_A)}$$

$$K_p = \frac{x \cdot x}{(P_0-x)}$$

at eqm

$P_A = P_0 - x$

$P_B = x$

$P_C = x$

Case-III → if initial moles and K_c is given

$$A \rightleftharpoons B + C$$

	A	B	C
t=0	n mol	0	0
t=eqm	n-x	x	x

$$K_c = \frac{[B][C]}{[A]} = \frac{x \cdot x}{n-x}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{n-x}{V}\right)}$$

→ if Vol is not given, then consider $V = 1\,l$

Case-IV → if initial moles and K_p are given

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$$

t=0	n	0	0
t=eqm	n-x	x	x

$$K_p = \frac{(P_B)(P_C)}{(P_A)} = \frac{\left(\frac{x}{n+x} \cdot P_{total}\right)\left(\frac{x}{n+x} \cdot P_{total}\right)}{\left(\frac{n-x}{n+x} \cdot P_{total}\right)}$$

at eqm $\Rightarrow n_{total} = n - x + x + x = n + x$

P_{total}

$$P_A = x_A \cdot P_{total} = \frac{n-x}{n+x} \times P_{total}$$

$$P_B = x_B \times P_{total} = \frac{x}{n+x} \cdot P_{total}$$

$$P_C = x_C \times P_{total} = \frac{x}{n+x} \cdot P_{total}$$

Dalton's law of Partial Pressure

↳ mixture of non-reactive gases.

↳ $P_A \propto x_A$

$$P_A = x_A \, P_{total} = \frac{n_A}{n_{total}} \times P_{total}$$

↳ Partial Pressure of A / individual Pressure of A

Degree of dissociation (α):- represent fraction of molecules undergoing dissociation from 1 mole of reactants.

↳ always in fraction $(0 \leq \alpha \leq 1)$

↳ Sometimes it is given in % $(0 \leq \alpha \leq 100\%)$

$$\frac{\alpha_{\%}}{100} = \alpha_{\text{fraction}}$$

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{initial moles taken}}$$

$$\alpha = \frac{M_T - M_O}{(n-1)M_O}$$

where M_T = Theoratical molar mass.

M_O = observed molar mass.

n = no. of particles after dissociation of 1 mole.

$$1\ PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$(n = 2)$

$$\alpha = \frac{D - d}{(n-1)d}$$

where D = Theoratical V.D

d = observed V.D

n = no. of particles after dissociation of 1 mole.

$A \rightleftharpoons B + C$			
t=0	1 mol	0	0
t=eqm	$1-\alpha$	α	α

$A \rightleftharpoons B + C$			
t=0	10 mol	0	0
t=eqm	$10-10\alpha$ (no stoichiometry)	10α	10α

$2P \rightleftharpoons 3C + R$			
t=0	10 mol	0	0
t=eqm	$10-10\alpha$ (no stoichiometry)	$\frac{30\alpha}{2}$	$\frac{10\alpha}{2}$ (stoichiometry Used)

Case-V → if initial moles and K_c are given
α = given

$$2P \rightleftharpoons 3C + 2R$$

t=0	n mol	0	0
t=eqm	$n - n\alpha$	$\frac{3n\alpha}{2}$	$n\alpha$

$n - n\alpha$ → no stoichiometry

$$K_c = \frac{[C]^3[R]^2}{[P]^2}$$

$$K_c = \frac{\left(\frac{n\alpha}{V}\right)^2\left(\frac{3n\alpha}{2V}\right)^3}{\left(\frac{n-n\alpha}{V}\right)^2}$$

Case-VI → if initial moles and α and K_p and P_{total} at eqm is given

$$2P_{(g)} \rightleftharpoons 3C_{(g)} + 2R_{(g)}$$

t=0	n mol	0	0	
t=eqm	$n - n\alpha$	$\frac{3n\alpha}{2}$	$n\alpha$	at eqm $n_{total} = n - n\alpha + \frac{3n\alpha}{2} + n\alpha = n\left(1 + \frac{3\alpha}{2}\right)$

$$P_C = x_C \times P_{total} = \frac{\left(\frac{3n\alpha}{2}\right)}{n\left(1+\frac{3\alpha}{2}\right)} \cdot P_{total} = \frac{\left(\frac{3\alpha}{2}\right)}{\left(1+\frac{3\alpha}{2}\right)} \cdot P_{total}$$

$$P_P = x_P \times P_{total} = \frac{n - n\alpha}{n\left(1+\frac{3\alpha}{2}\right)} \cdot P_{total} = \frac{1-\alpha}{\left(1+\frac{3\alpha}{2}\right)} \cdot P_{total}$$

$$P_R = x_R \times P_{total} = \frac{n\alpha}{n\left(1+\frac{3\alpha}{2}\right)} \cdot P_{total} = \frac{\alpha}{\left(1+\frac{3\alpha}{2}\right)} \cdot P_{total}$$

$$K_p = \frac{(P_C)^3(P_R)^2}{(P_P)^2}$$

Shortcut

$X_{(g)} \rightleftharpoons Y_{(g)} + Z_{(g)}$

$$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P_{total}$$

$P_{(g)} \rightleftharpoons 2R_{(g)}$

$$K_p = \frac{4\alpha^2}{1-\alpha^2} \cdot P_{total}$$

independent of no. of moles

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Le-chatlier's Principle ⇒ oppose the changes

$R \rightleftharpoons P$

① effect of conc^n

[P] ↓ or [R] ↑ = eqm will shift in forward direction.

[P] ↑ or [R] ↓ = eqm will shift in Backward direction.

② effect of Temp :- In general { Temp. ↑, eqm will shift in endothermic direction
Temp. ↓ eqm will shift in exothermic direction }

$R \rightleftharpoons P + Heat$ { → Forward → exothermic
→ Backward → endothermic }

Temp. ↑ = heat ↑ ⇒ eqm will shift in backward direction

Temp ↓ = heat ↓ ⇒ eqm will shift in forward direction.

③ Effect of Pressure or volume

Volume ↑ or Pressure ↓ ⇒ eqm will shift in more no. of gaseous moles side.

Volume ↓ or Pressure ↑ ⇒ eqm will shift in less no. of gaseous moles side.

> No effect of P/V if $\Delta n_g = 0$

④ Effect of Catalyst → No effect on (eqm) or (K_{eq})

- ↳ reduces the time to achieve eqm.
- ↳ increases rate of forward & Backward rxn by same amount.

⑤ effect of inert gas addition

- → at Constant volume ⇒ No effect.
- → at Constant Pressure ⇒ volume ↑ = eqm will shift in more gaseous moles side.

Homework

- PYQs
- NCERT


Thank you