CHEMICAL EQUILIBRIUM

→ It is a dynamic equilibrium.

Types of chemical Reactions :-

(a) On the basis of physical state

Homogenous Rxn

→ Reactant and Product are in same phase.

$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)}$

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

Heterogeneous Rxn

→ Reactant and product are in two or more phase.

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

$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

(b) On the basis of speed

Fast Rxn

→ Generally ionic reactions

$HCl + NaOH \rightarrow NaCl + H_2O$

→ Here rate determination is not possible.

Slow Rxn

→ Generally molecular reactions.

$H_2 + I_2 \rightleftharpoons 2HI$

→ Here rate determination is possible.

(c) On the basis of direction

(i) Irreversible Reaction

1. All combustion reactions are irreversible.

$CH_4 + O_2 \longrightarrow CO_2 + H_2O + \Delta$

2. All precipitation reactions are irreversible.

$NaCl + AgNO_3 \longrightarrow \underset{\text{white ppt}}{AgCl\downarrow} + NaNO_3$

3. All neutralisation (SA + SB) reactions are irreversible.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

4. Reactions in which any of the product escape as gas is irreversible.

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

5 All ionic redox reactions are irreversible.

$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

(ii) Reversible reactions

→ Reactant converts into product and vice-versa.

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

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

→ Possible in closed container.

→ Can attain equilibrium.

→ Neutralisation reactions except SA + SB.

$$HCl + NH_4OH \rightleftharpoons NH_4Cl + H_2O$$

Chemical Equilibrium

$$A + B \rightleftharpoons C + D$$

Initially 2 mole 2 mole

with time 't' 1 mole 1 Mole

Ex

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ (Haber's process)

$2SO_2 + O_2 \rightleftharpoons 2SO_3$ (contact process)

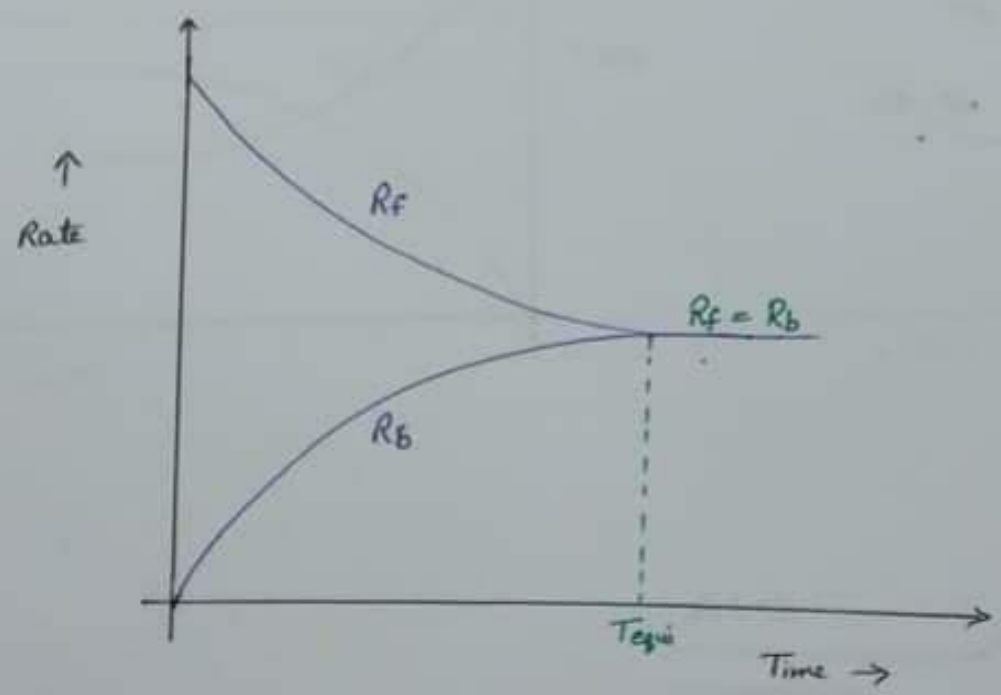
$2NO \rightleftharpoons N_2 + O_2$

$H_2 + I_2 \rightleftharpoons 2HI$

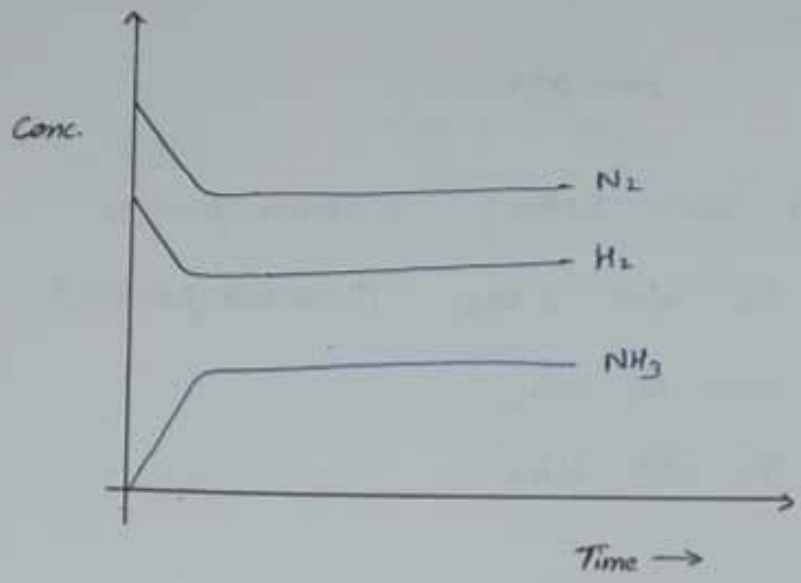
At Equilibrium

$$\boxed{\text{Rate of forward Rxn} = \text{Rate of backward Rxn}}$$

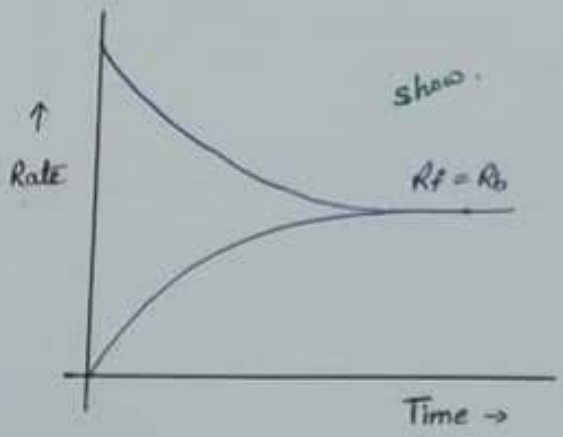
$$A \underset{R_b}{\overset{R_f}{\rightleftharpoons}} B$$

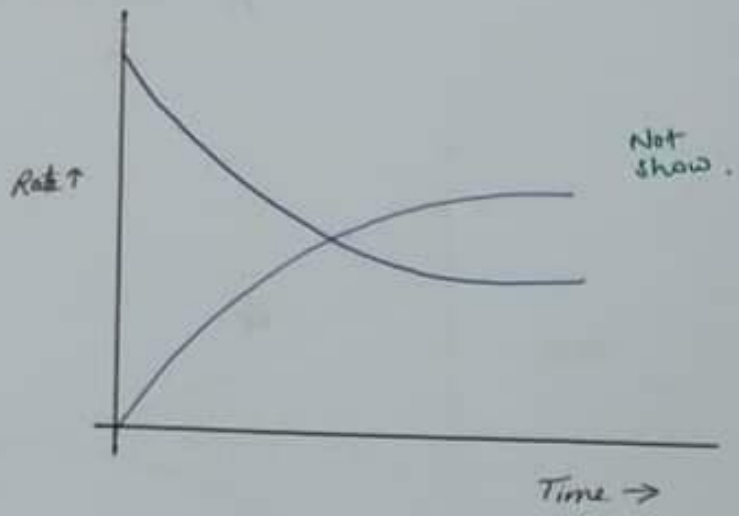


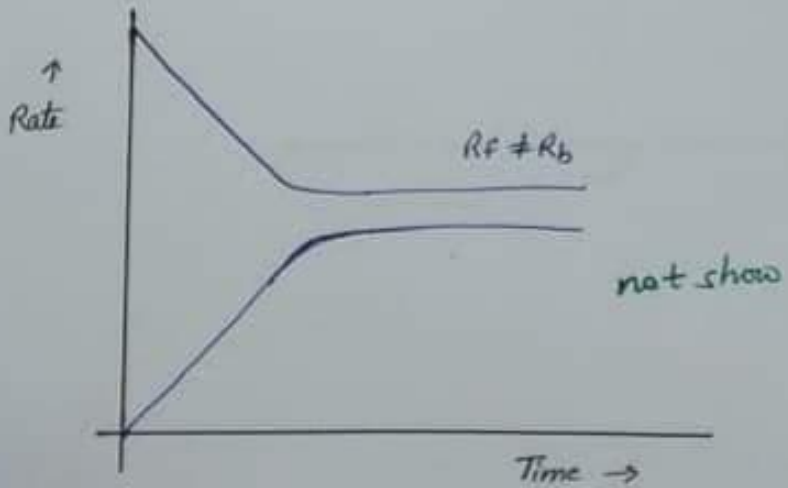
At equilibrium, concentration of R & P becomes constant and does not change with time.



Rate vs time Graph

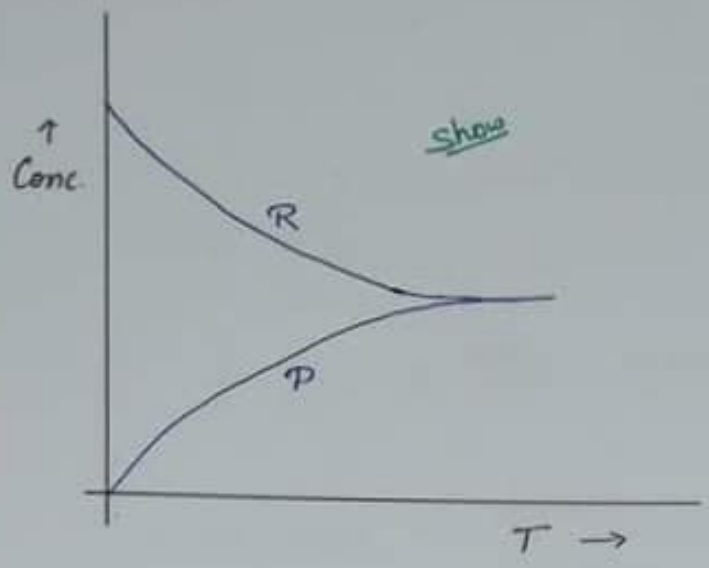






Concentration Vs Time Graph

Conc. must be constant of each term.



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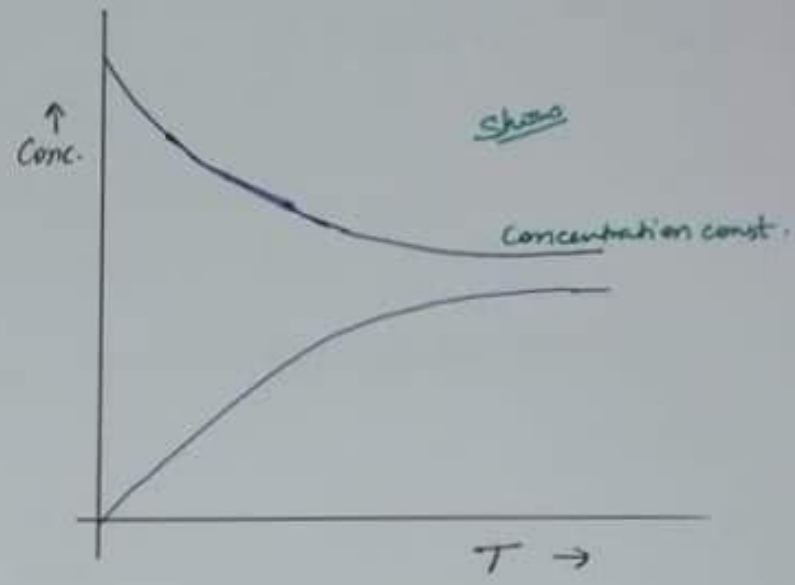

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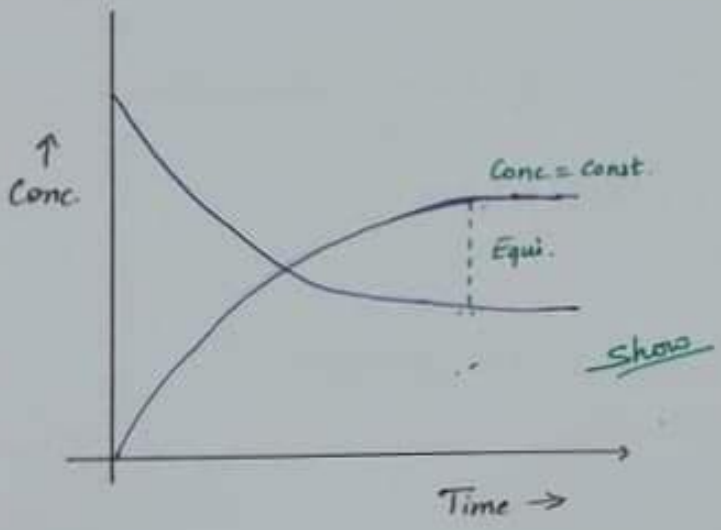

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Active mass [ ]

→ The concentration of reactants expressed in terms of molar concentration or mol/L.

$$[\ ] = \frac{n}{Vol.} = \frac{wt}{M.wt \times V_L} = \frac{wt \times 1000}{M.wt \times V_{ml}} = \frac{f}{M.wt} \times 100$$

f = density

[ ] → In molar conc. term ⟶ K_c

[ ] → In Gaseous system ⟶ K_p (Partial pressure)

$P \propto \frac{n}{V}$

$$\text{Active mass} = \frac{\text{density}}{\text{Mol. wt}} = \frac{f}{M.wt}$$

★ The active mass of solids and pure liquids are constant (unity).

$$[\text{Solid / Liquid}]^{\circ} = \text{Unity}.$$

Ex :-

(i) $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

$K_c = 4$

K_p = Not applicable.

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

$K_c = [CO_2]$

$K_p = P_{CO_2}$

(iii) $(NH_4)_2S_{(s)} \rightleftharpoons 2NH_{3(g)} + H_2S_{(g)}$

$K_p = P^2_{NH_3} \cdot P_{H_2S}$

Q. 8.5 gm NH_3 is present in a vessel of 0.5 L capacity then find out the active mass of NH_3 ?

$$[NH_3] = \frac{8.5}{17 \times 0.5} = 1 \text{ mol/L}.$$ Ans.

Characterstics of Chemical Equilibrium

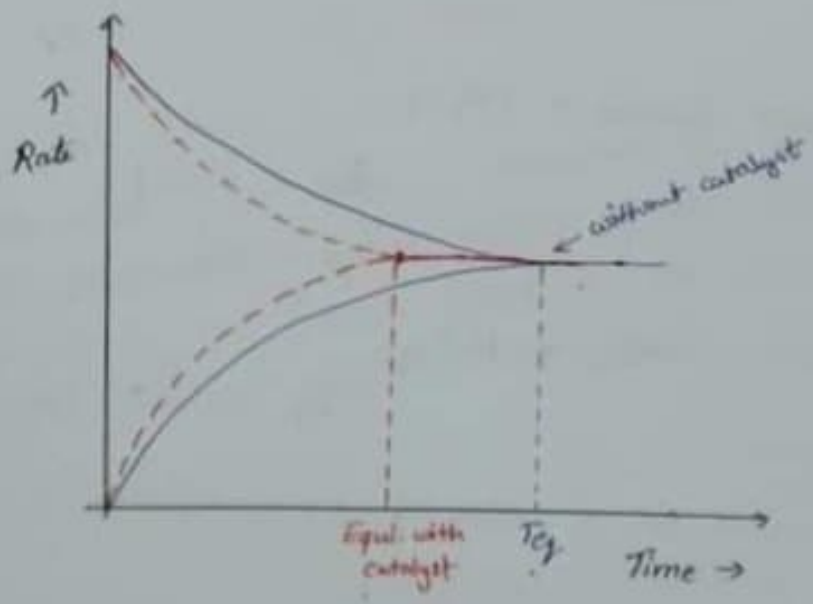
1. Dynamic in nature (Reaction doesn't stop).
2. At Equilibrium $R_f = R_b$.
3. Equilibrium can be achieved from any side.

$$N_2O_4 \rightleftharpoons 2NO_2$$

Colourless at 273K — Reddish brown at 373K

here reaction can be start from anywhere

4. Equilibrium attain in a closed container only.
5. Temperature must be constant.
6. All the measurable properties like concentration, Pressure, Num. of moles, density, colour etc. does not change with time and becomes constant.
7. Change in Temperature and Pressure effects the equilibrium state (Le-chatlier's law).
8. Catalyst has no effect on equilibrium state. It only helps to attain equilibrium earlier.



Law of Mass Action

→ Given by Guldberg and Waage.

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

Rate of forward Rxn $\propto [A]^a [B]^b$

Rate of backward Rxn $\propto [C]^c [D]^d$

Rate of forward Rxn $= K_f [A]^a [B]^b$

Rate of backward Rxn $= K_b [C]^c [D]^d$

$$R_f = R_b$$

$$K_f [A]^a [B]^b = K_b [C]^c [D]^d$$

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

$$\boxed{K_{eq} = \frac{K_f}{K_b} = \frac{[\text{Product}]}{[\text{Reactant}]}}$$

K_{eq} = Equilibrium const.

This law states that

" The rate of a chemical reaction is directly proportional to the product of active masses of the reacting substances raised to the power equal to the stoichiometric coefficient in a balanced chemical equation."

Ex $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_{eq} = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

K_{eq}

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad mol/L.$$

$$K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \quad atm.$$

<u>Examples</u>

$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

Physical Equilibrium

$$K_c = [H_2O]$$

the active mass of liquid with gas in equilibrium is taken unity.

$$K_p = P_{H_2O}$$

$Cu_{(s)} + Ag^+_{(aq)} \rightleftharpoons Cu^{++}_{(aq)} + 2Ag_{(s)}$

K_p = Not defined

(b/c valid for gases only)

★ K_p of solid always taken unity.

Application of Law of Mass action

Homogeneous Gaseous Reactions.

Type – I ($\Delta n_g = 0$)

Synthesis of HI

	H_2	$+ I_2$	$\rightleftharpoons 2HI$
initial mole	a	b	0
At Equilibrium	$a-\alpha$	$b-\alpha$	2α

Total volume is V. then active mass :-

$$\frac{a-\alpha}{V} \quad \frac{b-\alpha}{V} \quad \frac{2\alpha}{V}$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2\alpha}{V}\right)^2}{\left(\frac{a-\alpha}{V}\right)\left(\frac{b-\alpha}{V}\right)}$$

$$\boxed{K_c = \frac{4\alpha^2}{(a-\alpha)(b-\alpha)}}$$

when $a = b = 1$ & α = degree of formation of HI or diso. of H_2 & I_2.

$$\boxed{K_c = \frac{4\alpha^2}{(1-\alpha)^2}}$$

If $\alpha <<< 1$ then $1-\alpha \approx 1$

$$\boxed{K_c = 4\alpha^2}$$

$$\boxed{\alpha = \sqrt{\frac{K_c}{4}}}$$

* $\alpha \propto V^0$

** At equi, 'α' is independent of volume.

$$H_2 + I_2 \rightleftharpoons 2HI$$

$a-\alpha \qquad b-\alpha \qquad 2\alpha$

Total no. of moles $= a-\cancel{\alpha} + b-\cancel{\alpha} + \cancel{2\alpha}$

$= a+b$

$$\frac{a-\alpha}{a+b}P \quad \frac{b-\alpha}{a+b}\cdot P \quad \frac{2\alpha}{a+b}\cdot P$$

$$K_p = \frac{\left(\frac{2\alpha}{a+b}\right)^2 \cancel{P^2}}{\left(\frac{a-\alpha}{a+b}\right)\left(\frac{b-\alpha}{a+b}\right)\cancel{P^2}}$$

$$\boxed{K_p = \frac{4\alpha^2}{(a-\alpha)(b-\alpha)}}$$

Thus $K_p = K_c$

If $\alpha << 1$

$$\boxed{K_p = 4\alpha^2}$$

$$\boxed{\alpha = \sqrt{\frac{K_p}{4}}}$$

$\alpha \propto P^0$

** At Equi., 'α' is independent of Pressure.

Type - II ($\Delta n_g > 0$)

Dissociation of PCl_5

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

Initial	a	0	0
At Equi.	$a-x$	x	x
Active masses	$\frac{a-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_c = \frac{\frac{x}{V} \cdot \frac{x}{V}}{\frac{a-x}{V}}$$

$$\boxed{K_c = \frac{x^2}{(a-x)V}}$$

If $a = 1$, then

$$\boxed{K_c = \frac{x^2}{(1-x)V}}$$

$x <<< 1$ then $1 - x \approx 1$ $\quad$ x = degree of diso. of PCl_5

$$\boxed{K_c = \frac{x^2}{V}}$$

$$x^2 = V$$

$$x = \sqrt{V}$$

** At Equi, 'x' is directly proportional to the square root of volume.

Expression of K_p

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$a-x \qquad x \qquad x$$

Total moles $= a - \cancel{x} + \cancel{x} + x$

$= a + x$

$$K_p = \frac{\frac{\alpha}{a+\alpha} \cdot P \; \frac{\alpha}{a+\alpha} \cdot P}{\frac{a-\alpha}{a+\alpha} \cdot P}$$

$$\boxed{K_p = \frac{\alpha^2 \cdot P}{(a+\alpha)(a-\alpha)}}$$

If $a = 1$ then

$$\boxed{K_p = \frac{\alpha^2 P}{1-\alpha^2}}$$

If $\alpha << 1$ then $1-\alpha \simeq 1$

$$\boxed{K_p = \alpha^2 \cdot P}$$

$$\alpha \propto \frac{1}{\sqrt{P}}$$

** At Equi, 'α' is inversely proportional to the square root of Pressure.

$$\overset{1}{N_2} + \overset{3}{3H_2} \rightleftharpoons \overset{2}{2NH_3}$$

initial	a	b	
At Equi.	$a-\alpha$	$b-3\alpha$	2α
Active mass	$\frac{a-\alpha}{V}$	$\frac{b-3\alpha}{V}$	$\frac{2\alpha}{V}$

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

$$\boxed{K_c = \frac{4\alpha^2 V^2}{(a-\alpha)(b-3\alpha)^3}}$$

If $a=1, b=1$

$$K_c = \frac{4\alpha^2 V^2}{(1-\alpha)(1-3\alpha)^3}$$

$$\boxed{K_c = \frac{4\alpha^2 V^2}{27(1-\alpha)^4}}$$

$\alpha <<< 1$ then $1-\alpha \approx 1$

$$\boxed{K_c = \frac{4\alpha^2 V^2}{27}}$$

$$K_c = \alpha^2 V^2$$

$$\alpha \propto \frac{1}{\sqrt{V}}$$

At Equi, 'α' is inversely proportional to the volume of vessel.

Expression of K_p

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

$$a-\alpha \qquad b-3\alpha \qquad 2\alpha$$

Total no. of moles $= a-\alpha + b-3\alpha + 2\alpha$

$= a+b-2\alpha$

$$\frac{a-\alpha}{a+b-2\alpha}\cdot P \qquad \frac{b-3\alpha}{a+b-2\alpha}\cdot P \qquad \frac{2\alpha}{a+b-2\alpha}\cdot P$$

$$K_p = \frac{\left(\frac{2\alpha}{a+b-2\alpha}\right)^2 P^2}{\left(\frac{a-\alpha}{a+b-2\alpha}\cdot P\right)\left(\frac{b-3\alpha}{a+b-2\alpha}\cdot P\right)^3}$$

$$K_p = \frac{4\alpha^2 (a+b-2\alpha)^2}{(a-\alpha)(b-3\alpha)P^2}$$

If $a=1, b=3$

$$\boxed{K_p = \frac{16\alpha^2 (2-\alpha)^2}{27(1-\alpha)^4 \cdot P^2}}$$

$\alpha <<< 1$. then $2-\alpha \approx 2$

$1-\alpha \approx 1$

$$\boxed{K_p = \frac{64\alpha^2}{27P^2}}$$

$$\alpha^2 \propto P^2$$

** At Equi, 'α' is directly proportional to the pressure.