

Chemical Eq^m

Types of reaction

Based on physical State

- ① Homogeneous Reaction
- ② Heterogeneous Reaction

Based on heat involved

- ① Endothermic
- ② Exothermic

Based on direction

- ① Reversible
- ② Irreversible

Homogeneous reaction: All reactant & product are in same phase. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Heterogeneous reaction: Reactant & product are in more than one phase.



Exothermic rxⁿ: Heat is released in the reaction. $\Delta H = -ve$, $R \rightarrow P + x \text{ kcal (release)}$

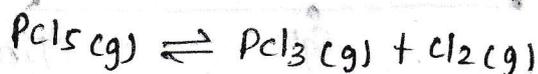
Endothermic rxⁿ: Heat is absorbed in this reaction. $\Delta H = +ve$, $R + x \text{ kcal} \rightarrow P$

Reversible

- Products Can be converted back into reactant.

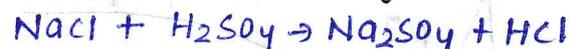
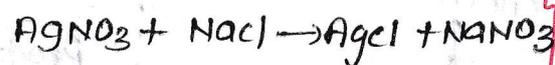


- Proceed in forward/backward reaction
- attain the equilibrium state & never completes.
- Generally possible closed contain.

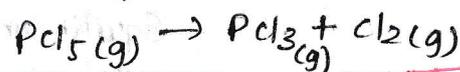


Irreversible

- Products Cannot be converted back into reactant.



- proceed in only one direction.
- Reaction completes & do not attain eq^m.
- occurs in open container also



EQUILIBRIUM

It is a state of reversible process, in which properties of reactant & product do not change with time.

Static Eq^m

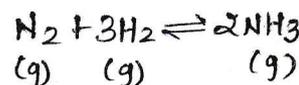
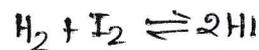
X

Dynamic Eq^m

Physical Equilibrium

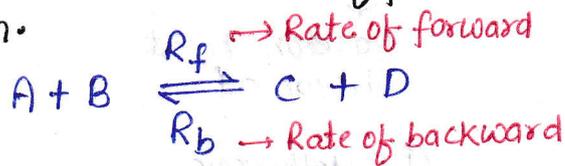
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Chemical Equilibrium



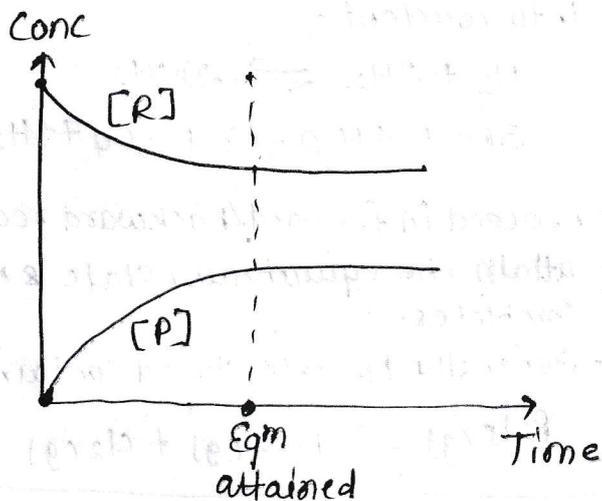
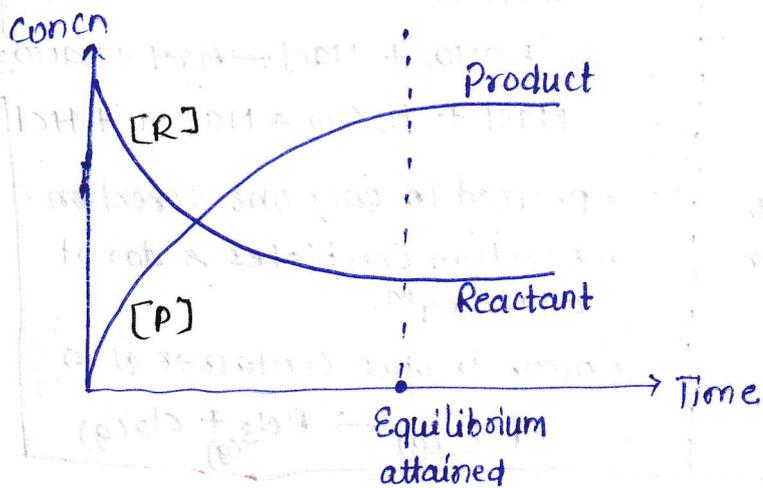
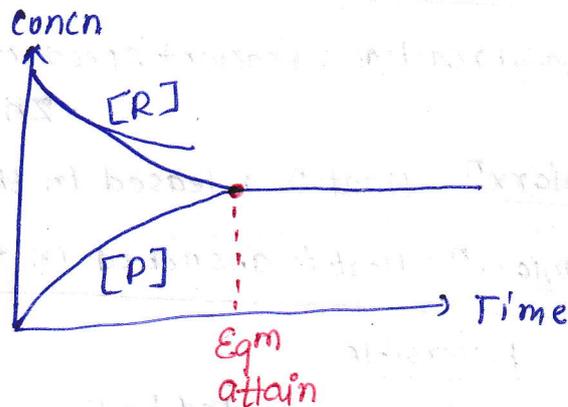
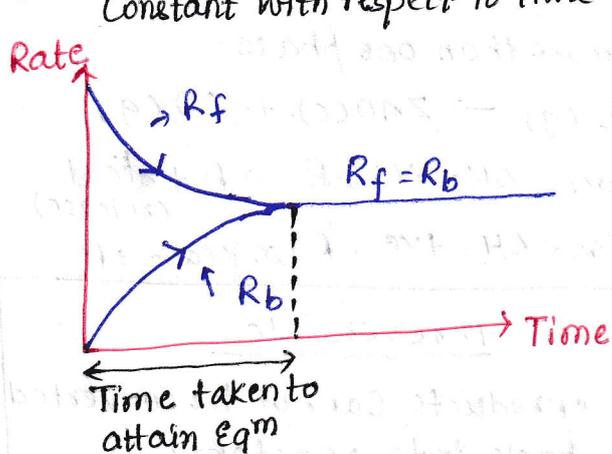
Chemical Eq^m

Reversible reaction in which rate of forward reaction is equal to rate of backward reaction.



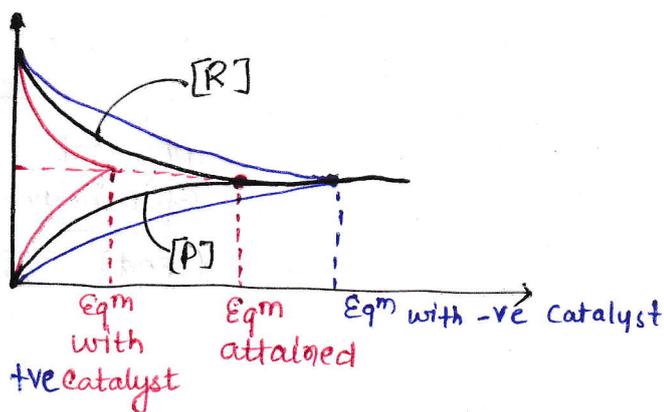
at Equilibrium $R_f = R_b$

Reversible reaction in which concentration of reactant & product remain constant with respect to time.



Use of Catalyst

Catalyst alters the rate of approach of Eq^m but do not change the state of Equilibrium.



Equilibrium state can be affected only by alternating factors :-
eg: pressure, vol, concentration, temp etc (Lechatelier's principle)

Law of mass action & Equilibrium Const

(2)

Law of mass action: Rate of a chemical reaction at particular temp is directly proportional to product of active masses of reactant raised to the power of their stoichiometric coefficient.



$$r_f = k_f [A]^a [B]^b \quad \Bigg| \quad r_b = k_b [C]^c [D]^d$$

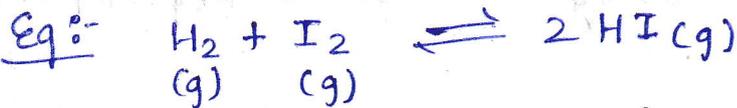
at Eq^m $r_f = r_b$

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

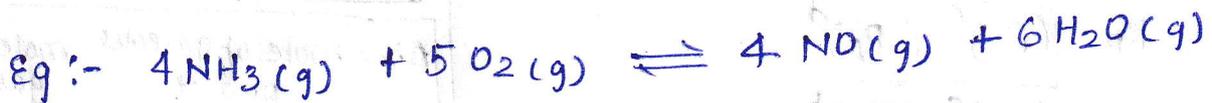
$$\frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

Eq^m Constant



$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$



$$K_c = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5}$$

Eq^m const

K_c
(when concentration of reactant & product is used)

K_p
(when partial pressure of reactant & product is used)



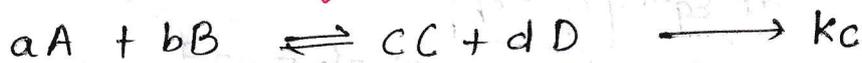
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

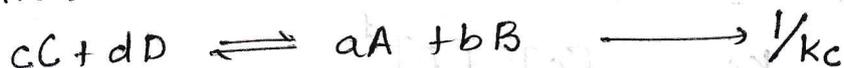
- equilibrium constant only depends on temperature & it is independent of everything.

Ques → NCERT Ques

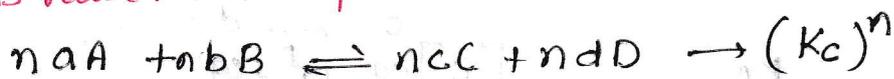
Relation of equilibrium constant



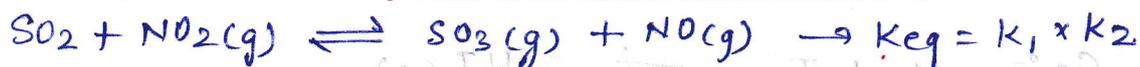
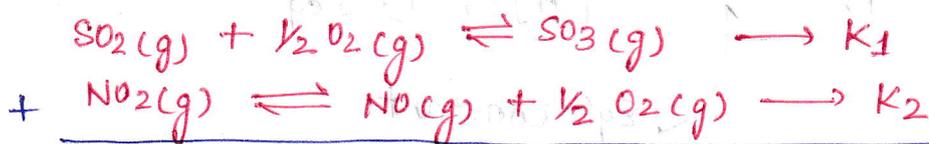
- (i) if reaction is reverse then K_c becomes reciprocal



- (ii) if a reaction is multiplied by any number then value of equilibrium constant is raised to that power



- (iii) if two reactions are added then eq^m constant is multiplied.



Ques → NCERT Ques

Relation b/w K_p & K_c



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

$$PV = nRT$$

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

$$P = CRT$$

$$K_p = \frac{[C]^c [D]^d (RT)^c (RT)^d}{[A]^a [B]^b (RT)^a (RT)^b}$$

$$K_p = K_c (RT)^{(c+d-a-b)}$$

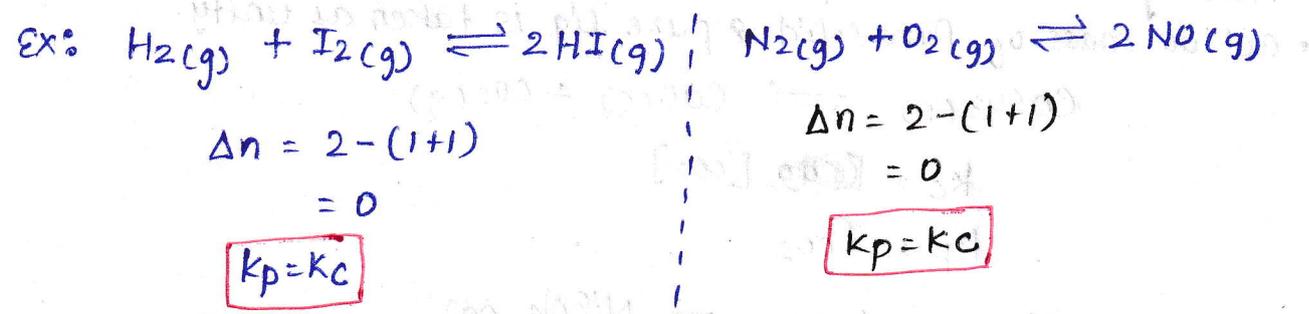
$$K_p = K_c (RT)^{\Delta n}$$

$\Delta n = \text{moles of gaseous product} - \text{moles of gaseous reactant}$

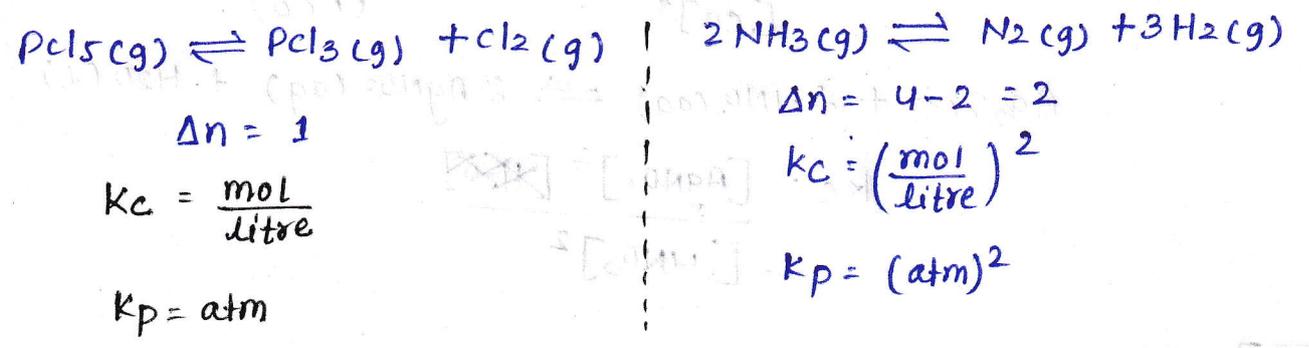
unit of $K_c \rightarrow \left(\frac{\text{mol}}{\text{litre}}\right)^{\Delta n}$

unit of $K_p \rightarrow (\text{atm})^{\Delta n}$

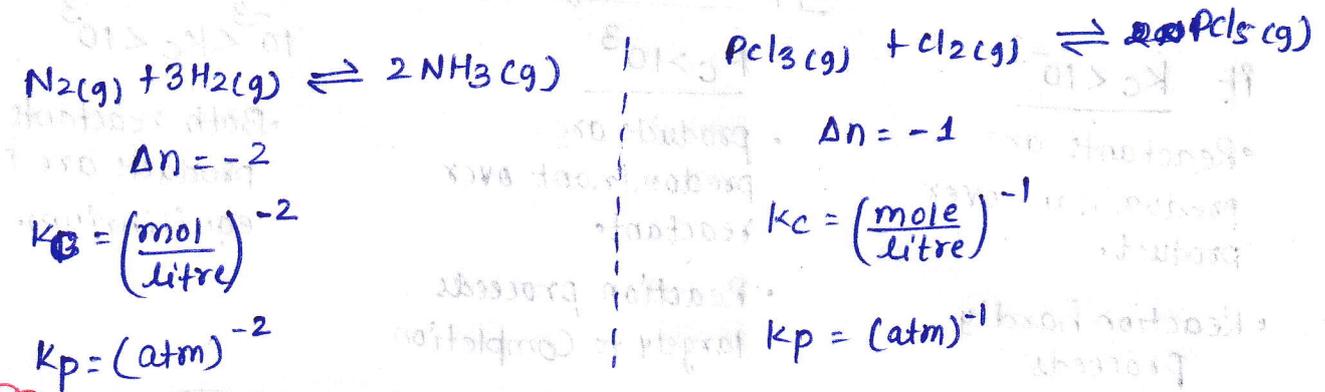
Case 1: $\Delta n = 0$ $K_p = K_c(RT)^0 \Rightarrow K_p = K_c \Rightarrow K_p \& K_c$ are unitless



Case 2: $\Delta n = +ve$ $K_p = K_c(RT)^{\Delta n} \Rightarrow K_p > K_c$



Case 3: $\Delta n = -ve$ $K_p = K_c(RT)^{\Delta n} \Rightarrow K_p < K_c$

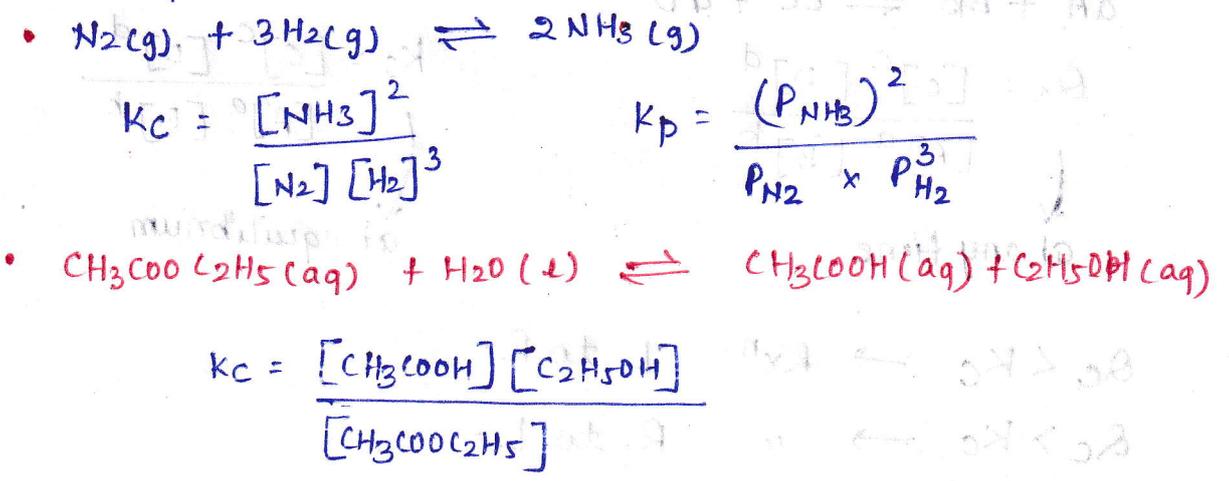


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Homogeneous & Heterogeneous Eqm

Homogeneous Equilibrium

all the reactant & product are in same phase.



Heterogeneous Eq^m

- Having more than one phase
- active mass of Pure solid & pure liq is taken as unity.



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

$$K_p = P_{\text{CO}_2}$$



$$K_c = \frac{[\text{Ni}(\text{CO})_4]}{[\text{CO}]^4}$$

$$K_p = \frac{P_{\text{Ni}(\text{CO})_4}}{(P_{\text{CO}})^4}$$



$$K_c = \frac{[\text{AgNO}_3]^2 [\text{H}_2\text{O}]}{[\text{HNO}_3]^2}$$

Que →

Application of Eq^m Const

if $K_c < 10^{-3}$

- Reactants are predominant over product.
- Reaction hardly proceeds

$K_c > 10^3$

- products are predominant over reactant.
- Reaction proceeds largely to completion.

$10^{-3} < K_c < 10^3$

- Both reactants & products are in equilibrium.

Predicting the direction of Reaction

Q_c → Reaction Quotient



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

at any time

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

at equilibrium

$Q_c < K_c \rightarrow R \rightarrow L$

$Q_c > K_c \rightarrow L \rightarrow R$

$Q_c = K_c \rightarrow$ no net reaction occurs.

→ Que →

Relⁿ b/w Eq^m Const K, Reaction Quotient Q, Gibbs free Energy G (4)

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

at Eq^m $\Delta G = 0$ & $Q = K_c$

at Eq^m $\Rightarrow \Delta G^\circ = -RT \ln K_c$

$$\ln K_c = \frac{-\Delta G^\circ}{RT}$$

$$K_c = e^{-\Delta G^\circ/RT}$$

$\Delta G^\circ < 0 \rightarrow K_c > 1 \rightarrow$ Spontaneous rxⁿ \rightarrow product is predominant

$\Delta G^\circ > 0 \rightarrow K_c < 1 \rightarrow$ non Spontaneous rxⁿ \rightarrow Reactant is predominant

Que

Degree of dissociation

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

$$\% \alpha = (\quad) \times 100$$

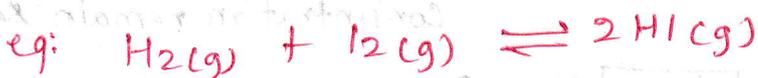
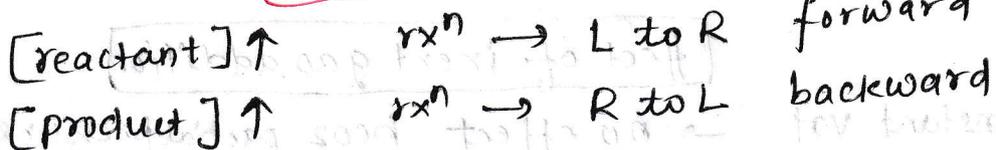
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Factors affecting Eq^m

Lechatelier principle

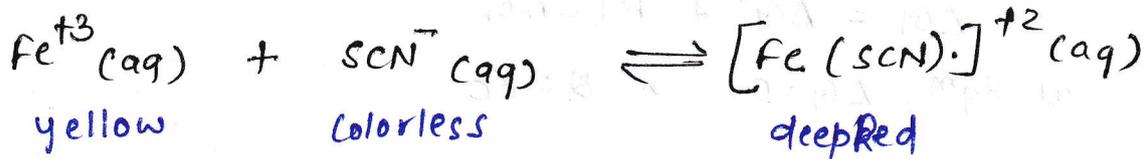
If Eq^m is subjected to change of Conc, press, temp then Eq^m is shifted in such a way to counter the effect of change & Eq^m is established again in new condⁿ.

Concentration change



If H_2 is added \rightarrow rxⁿ \rightarrow forward

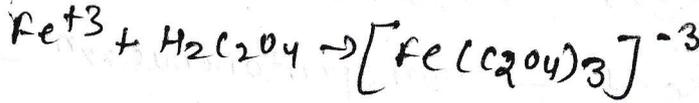
Experiment of Concentration change



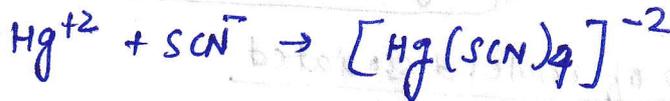
$$K_c = \frac{[\text{Fe}(\text{SCN})]^{+2}}{[\text{Fe}^{+3}][\text{SCN}^{-}]}$$

Addition of potassium thiocyanate \Rightarrow forward shift \Rightarrow Red color intensity increases.

Addition of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) \rightarrow Backward shift \rightarrow bcoz oxalic acid reacts with Fe^{+3} . So, reactant concentration \downarrow and hence rxn shifts backward.



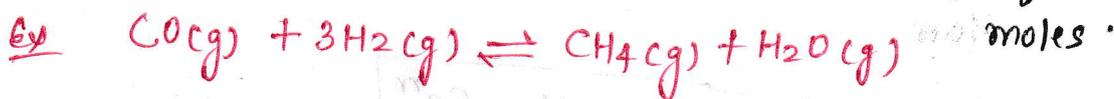
Addition of $\text{HgCl}_2 \rightarrow$ Backward shift \rightarrow red color intensity decreases.



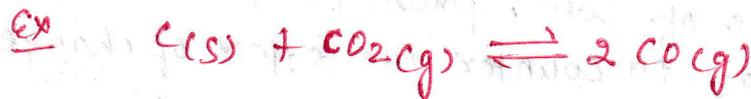
Effect of Pressure change

$P \uparrow \quad V \downarrow \Rightarrow C \uparrow \Rightarrow n \uparrow \rightarrow$ To counter it Eq^m shifts in direction of lower number of moles.

$\hookrightarrow C = \frac{n}{V}$



$P \uparrow \quad V \downarrow \quad C \uparrow \rightarrow n \uparrow \rightarrow$ rxn forward (lower mole).



$P \uparrow \quad V \downarrow \quad C \uparrow \rightarrow n \uparrow \rightarrow$ rxn backward (lower gas moles)

Effect of inert gas addition

at constant vol \rightarrow no effect bcoz partial pressure or molar concentration remain same.

at constant pressure \rightarrow $V \propto n$ $n \uparrow \quad V \uparrow \quad C \downarrow \quad n \downarrow$
eq^m shift towards larger no of mole

$\Delta n > 0$ $n_{\text{prod}} > n_{\text{Reactant}}$ rxn moves forward
 $\Delta n < 0$ " " " " " " backward
 $\Delta n = 0$ no effect.

Temp change

Endothermic

$\Delta H = +ve$

Von't Hoff equation

$\log \frac{k_2}{k_1} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

$T \uparrow$ $T_2 - T_1 = +ve$
 $\Delta H = +ve$

$\log \frac{k_2}{k_1} = +ve$

$\log \frac{k_2}{k_1} > 0$

$\log k_2 - \log k_1 > 0$

$\log k_2 > \log k_1$

$k_2 > k_1$

$T \uparrow$ $K \uparrow$
 rxn forward

Exothermic

$\Delta H = -ve$

$\log \frac{k_2}{k_1} = \frac{\Delta H}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$

$T \uparrow$ $T_2 - T_1 = +ve$
 $\Delta H = -ve$

$\log \frac{k_2}{k_1} = -ve$

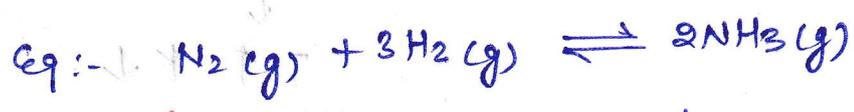
$\log \frac{k_2}{k_1} < 0$

$\log k_2 - \log k_1 < 0$

$\log k_2 < \log k_1$

$k_2 < k_1$

$T \uparrow$ $K \downarrow$
 rxn backward



$\Delta H = -92.38 \text{ kJ/mol}$
 exothermic

$T \uparrow$ rxn backward
 $k \downarrow \Rightarrow \text{Eq}^m \text{ conc of ammonia } \downarrow$

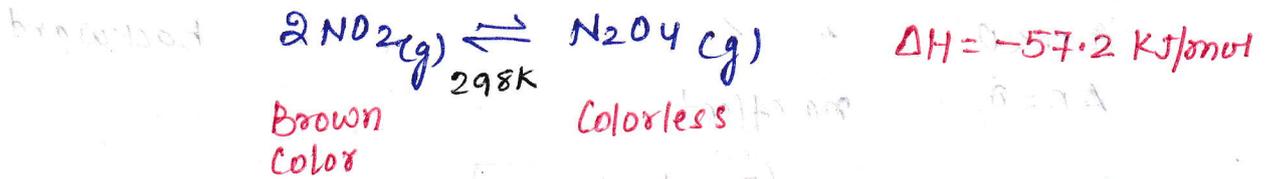
$T \downarrow$ $k \uparrow$ rxn forward $\Rightarrow \text{Eq}^m \text{ conc of ammonia } \uparrow$

$P \uparrow \rightarrow \text{Eq}^m \text{ shifts towards lower moles.}$

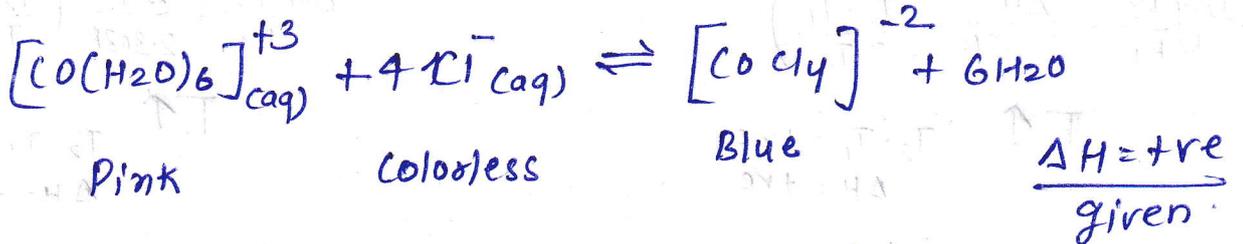
NH_3 formation favor \rightarrow Low temp & High Pressure.

\Rightarrow Low temp favours NH_3 formation but rxn slows down. so catalyst is needed.

Temp change \rightarrow Experiment



if Temp \uparrow $K \downarrow$ \Rightarrow intensity of Brown color \uparrow
 if Temp \downarrow $K \uparrow$ \rightarrow " " " " \downarrow



Temp \uparrow $K \uparrow$ \Rightarrow Blue color intensity \uparrow
 Temp \downarrow $K \downarrow$ \Rightarrow " " " " \downarrow

Effect of Catalyst

- State of Equilibrium donot changes.
- Catalyst lowers the activation energy for the forward & reverse rxn so, Eqm is achieved easily.



\downarrow
Exothermic

\downarrow

$T \uparrow$ $K \downarrow$

Low temp is fav for NH_3 formation
 but reaction slows down.

So, Catalyst is needed,
 \downarrow
 Iron Catalyst