CHAPTER # 7
(CHEMICAL EQUILIBRIUM)

IRREVERSIBLE REACTION	REVERSIBLE REACTION
• **Def:** "These are the reactions in which products cannot react together to form original reactants under same conditions."	• **Def:** "The reactions in which products can react together to form original reactants under same conditions are called reversible."
• **Direction:** They are uni-directional.	• **Direction:** They are bi-directional.
• **Limiting reactant concept:** Limiting reactant concept is applicable in irreversible reactions.	• **Limiting reactant concept:** Limiting reactant concept is not applicable in reversible reactions.
• **Representation:** It is represented by an arrow heading towards the direction of reaction. reactants ($\longrightarrow$) products	• **Representation:** It is represented by double arrow between reactants and products. reactants ($\rightleftharpoons$) products
• **End point:** The reactions almost go to completion in irreveribble reaction.	• **End point:** In reversible reactions, reactions do not go to completion.
• **Location:** These reactions are generally carried out in an open place.	• **Location:** These reactions are generally carried out in a closed container.

Muhammad Javed Iqbal
HOD Chemistry
Askaria Colleges Rwp.

Irreversible Reaction	Reversible Reaction
• **Equilibrium State:** Equilibrium state cannot be achieved in irreversible reactions.	• **Equilibrium state:** Equilibrium state is achieved in reversible reactions, where concentration of reactants and products become constant.
• **Examples:**	• **Examples:**
(i) $2Na + 2H_2O \longrightarrow 2NaOH + H_2$	(i) $H_2 + I_2 \rightleftharpoons 2HI$
(ii) $2H_2 + O_2 \longrightarrow 2H_2O$	(ii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

EQUILIBRIUM STATE
OR
DYNAMIC EQUILIBRIUM

• **Definition:**

"State at which rate of forward reaction become equal to rate of backward reaction is called equilibrium state."

OR

"State at which concentration of reactants and products become constant is called equilibrium state."

Characteristics:

1. At equilibrium state, concentration of reactants and products becomes constant.
2. When catalyst is added at start of reaction, it decreases time to achieve equilibrium state for that reaction but it has no effect on equilibrium state.
3. At equilibrium state, reaction appears to stoped but it does not stop and contineus at microscopic level. Individual molecules of reactants continues to combine. Similarly, individual molecules of products also conitnues to combine but at equal rate, so, reaction appears to be stopped.

Conditions:

1. Equilibrium state cannot be achieved in an open environment.
2. To achieve equilibrium state, Temperature, pressure and concentration should not be changed. The initial concentration of reactants and the products concentration should not be changed from outside.

Muhammad Javed Iqbal
HOD Chemistry
Askaria Colleges Rwp.

Explaination:

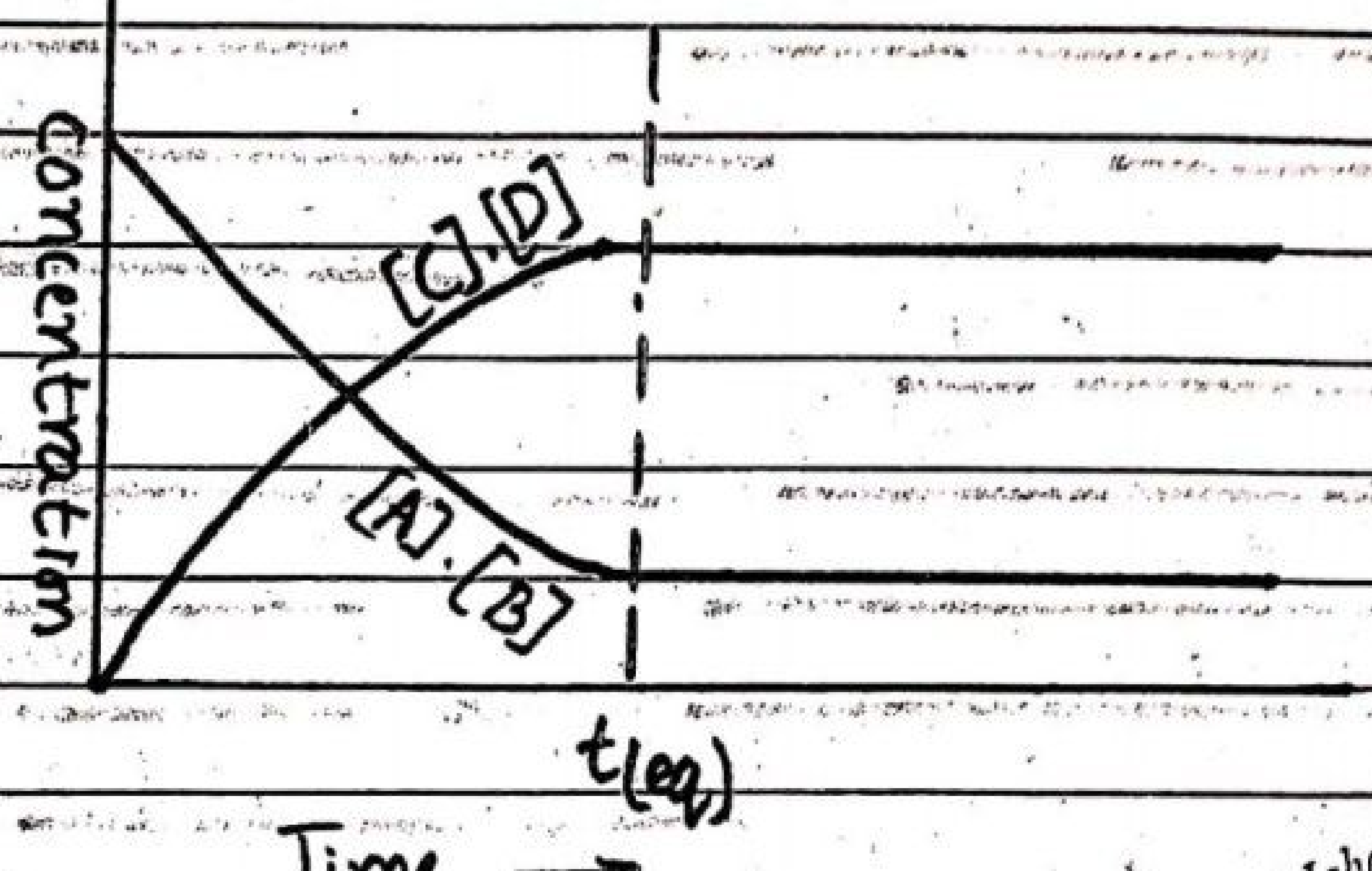
In the begining of reaction, concentration of reactants is maximum while concentration of products is zero.

As reaction proceeds, concentration of reactants decreases with time and concentration of products increases with time.

After some time, concentration of reactants and concentration of products becomes constant. At this state, there is no change in concentrations is observed. This state is is called equilibrium state or dynamic state.

- Graphical representation:

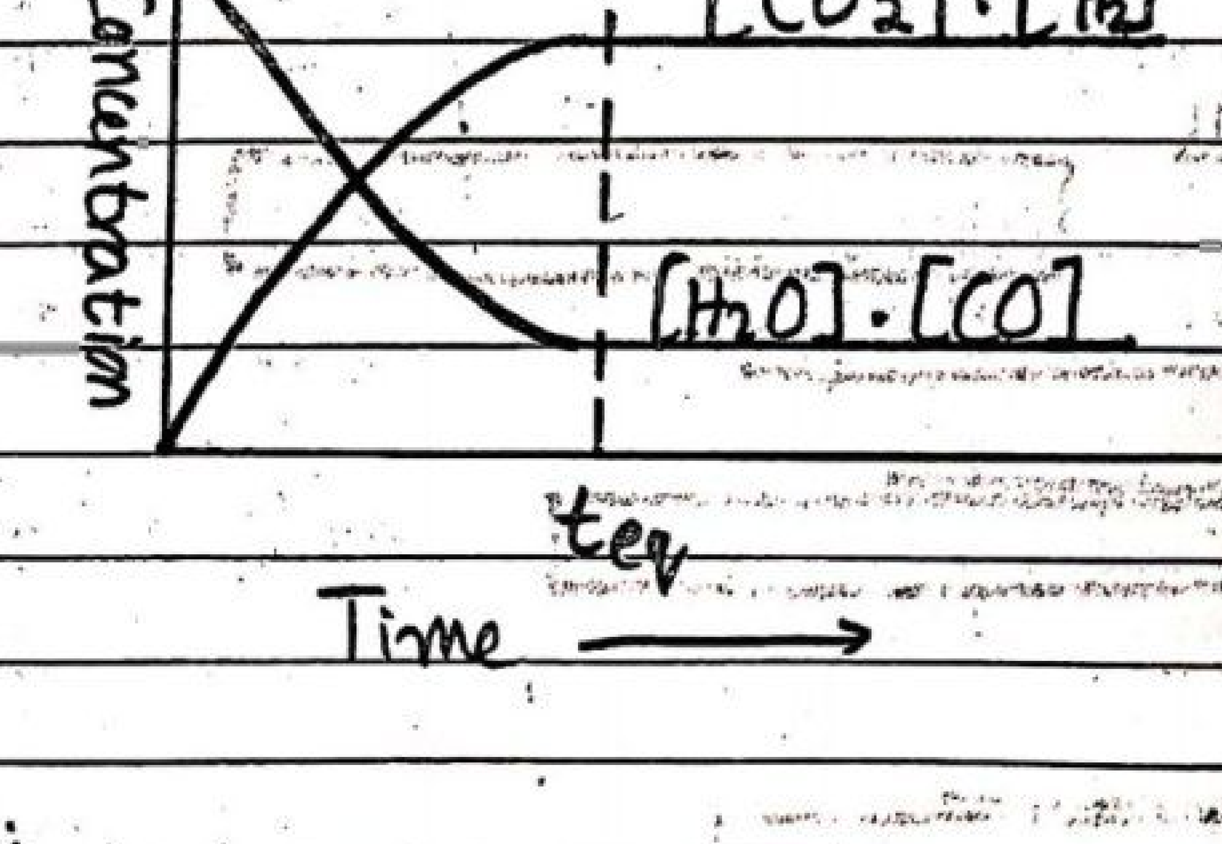
For,
$A + B \rightleftharpoons C + D$



t_{eq}:
The time at which reaction reaches the equilibrium state.

- Example:

$$H_2O + CO \rightleftharpoons CO_2 + H_2$$



At beginning:
In beginning of reaction, concentration of reactants ($H_2O + CO$) is maximum and concentration of products ($CO_2 + H_2$) is zero.

As reaction extends:
As reaction proceeds, concentration of $[H_2O]\cdot[CO]$ decreases and concentration of $[CO_2]\cdot[H_2]$ increases.
At equilibrium:
After sometime, concentration of $[H_2O]\cdot[CO]$ and concentration of $[CO_2]\cdot[H_2]$ become constant. At this stage (t_{eq}), equilibrium is established.

LAW OF MASS ACTION

OR

EQUILIBRIUM CONSTANT (K_c)

- **History:**
This law was proposed by P.Waage and Guldberg in 1864.
- **Definition:**
"According to this law, rate of reaction is directly propotional to product of active masses of the reacting substances."
- **Active mass:**
Definition: "Concentration of reactants and products in mol dm^{-3} for a dilute solution is called active mass."
- **Explaination:**
For a general reversible reaction.

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

where A and B are reactants and a, b are their no. of moles respectively. Similarly, C and D are products, c and d are their no. of moles respectively.

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

Rate of forward reaction $= K_f [A]^a [B]^b$ —— (1)

→ K_f:- rate constant for forward reaction.

Rate of Reverse reaction $\propto [C]^c [D]^d$

Rate of reverse reaction $= K_r [C]^c [D]^d$ —— (2)

→ K_r:- rate constant for reverse reaction.

At equilibrium:

Rate of forward reaction = Rate of Reverse reaction

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

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

$$\left[\frac{K_f}{K_r} = K_c\right] \qquad \therefore K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Where K_c is calle equilibrium constant.

- **Definition of K_c:**

"It is defined as the ratio between rate constant for forward reaction and rate constant for reverse reaction"

Mathematically:

$$K_c = \frac{\text{Rate constant for forward reaction}}{\text{Rate constant for reverse reaction}} = \frac{K_f}{K_r}$$

OR

- **Definition of K_c:**

"It is the ratio between concentration of products and concentration of reactants"

Mathematically:

$$K_c = \frac{[Product]}{[Reactant]}$$

- Explaination:

(i) Value of K_c depends upon temperature. Its value increases with increase in temperature and vice versa.

(ii) $K_c = 1$

If K_c of reaction is 1, Concentration of reactants and products are equal.

(iii) $K_c < 1$

If K_c of reaction is less than 1, concentration of reactant is greater than concentration of product.

(iv) $K_c > 1$

If K_c of reaction is greater than 1, concentration of product is greater than concentration of reactant.

- Example:

(i) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

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

(ii) $H_2O + CO \rightleftharpoons H_2 + CO_2$

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

(iii) $PCl_3 + Cl_2 \rightleftharpoons PCl_5$

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]}$$

(iv) $N_2O_4 \rightleftharpoons 2NO_2$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

• Unit of K_c:

(i) There is no unit of K_c when no. of moles of reactant and product are equal.

e.g;

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

$$K_c = \frac{[H_2][CO_2]}{[H_2O][CO]}$$

$$K_c = \frac{(\cancel{mol}\,\cancel{dm^{-3}})\ (\cancel{mol}\,dm^{-3})}{(\cancel{mol}\,dm^{-3})\ (\cancel{mol}\,dm^{-3})}$$

$$K_c = \text{no units}$$

(ii) There is unit of K_c when no. of moles of reactant and product are different.

e.g;

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

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

$$K_c = \frac{\cancel{(mol\,dm^{-3})^2}}{(mol\,dm^{-3})\ (mol\,dm^{-3})^{\cancel{3}}}$$

$$K_c = \frac{1}{(mol\,dm^{-3})\ (mol\,dm^{-3})}$$

$$K_c = mol^{-2}\,dm^{+6}$$

Relationship Between K_c, K_p, K_x, K_n
OR
Equilibrium Expresions Involving Partial Pressure, Mole Fraction & No. Of Moles

K_c: Equilibrium constant in terms of molar conc.

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC + dD$$

Suppose, the above general reaction is balanced and is in equilibrium. Equilibrium constant for above reaction would be written as.

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

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HOD Chemistry
Askaria Colleges Rwp.

The square bracket [ ] represents the concentration in $mol\,dm^{-3}$

Kp: Equilibrium constant in terms of partial pressure

When pressure is kept constant, the partial pressure of a gas is directly propotional to molar concentration. When concentrations are expressed in terms of partial pressure, the equilibrium constant would be.

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

Where P_A, P_B, P_C and P_D are partial pressure of gas A, B, C and D respectively

Relationship between K_c and K_p:

$$K_p = K_c (RT)^{\Delta n} \quad \text{---} (1)$$

where R : Ideal gas constant.
T : Temperature
Δn : difference between total no. of moles of products and total no. of moles of reactants $(nP - nr)$

If np and nr are same, then there is $\Delta n = 0$ and K_p would be equal to K_c ($K_p = K_c$)

K_x: Equilibrium constant in terms of mole fraction.

When equilibrium concentrations are expressed in terms of mole fraction, then equilibrium constant is given by-

- **Representation:**

K_x

- **Mathematically:**

$$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b}$$

Where X_A, X_B, X_C and X_D are mole fraction of gas A, B, C and D respectively.

- **Relationship between K_x and K_p:**

$$K_p = K_x (P)^{\Delta n} \quad \text{---} (2)$$

where P : Pressure of equilibrium mixture.

K_n: Equilibrium CONSTANT in terms of moles

When equilibrium concentrations of reactants and products are expressed in terms of their moles, then equilibrium constant is described below.

- **Representation:**

K_n

- **Mathematically:**

$$K_n = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b}$$

- **Relationship b/w K_p and K_n:**

$$K_p = K_n \left(\frac{P}{N}\right)^{\Delta n} \quad \text{—— ③}$$

where P: Pressure of equilibrium mixture
N: Total no. of moles of reactants and products

Conclusion

equ ①, ② and ③ are related as

$$K_p = K_c (RT)^{\Delta n} = K_x (P)^{\Delta n} = K_n \left(\frac{P}{N}\right)^{\Delta n}$$

If there is no difference between no. of moles of reactants and products ($\Delta n = 0$) then;

$$K_p = K_c (RT)^0 = K_x (P)^0 = K_n \left(\frac{P}{N}\right)^0$$

$$K_p = K_c (1) = K_x (1) = K_n (1)$$

$$\boxed{K_p = K_c = K_x = K_n}$$

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HOD Chemistry
Askaria Colleges Rwp.

TYPES OF EQUILIBRIUM

On the basis of physical state, there are two types of equilibrium

(i) Homogeneous Equilibria
(ii) Heterogeneous Equilibria

Homogenous Equilibria

Def: "Equilibrium system in which physical states of all reactants and products are same is called homogeneous equilibria"

Example:

$$\underset{(g)}{N_2} + \underset{(g)}{3H_2} \rightleftharpoons \underset{(g)}{2NH_3}$$

Hetergenous equilibria

Def: "Equilibrium system in which physical state of reactant and product are different is called heterogeneous equilibria"

Example:

$$\underset{(s)}{CaCO_3} \rightleftharpoons \underset{(s)}{CaO} + \underset{(g)}{CO_2}$$

If any of reactants or products has solid or liquid state in equilibrium mixture, it will not be included in equilibrium constant expression. This is because the concentration changing of solids or liquids will not effect the equilibrium system

e.g:

(i) $$\underset{(l)}{2H_2O} \rightleftharpoons \underset{(g)}{2H_2} + \underset{(g)}{O_2}$$

$$K_c = [H_2]^2 [O_2]$$

$$K_p = P^2_{H_2} \cdot P_{O_2}$$

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

$$K_c = \frac{[H_2]^4}{[H_2O]^4} , \quad K_p = \frac{P^4_{H_2}}{P^4_{H_2O}}$$

Ways To Recognize Chemical Equilibrium And Determination Of Equilibrium Constant

Equilibrium constant can be determined by to ways

(i) Physical method
(ii) Chemical method

(i) Physical method :-

→ It is also called spectrometric method.
→ Based on physical property of reactants and products
→ This method is applicable when a reactant or product absorbs light energy
→ Absorption of light is directly proportional to concentration
→ As reaction progresses, absorption of light at product side increases and at reactant side, it decreases.
→ At a particular time, absorption of light would be constant at regular intervals. So, it is concluded that equilibrium is established.

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HOD Chemistry
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e.g: $N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$2NO_2$
$t=0$	a mole	zero mol
$t=t_{eq}$	$\frac{a-x}{V}$ mol	$\frac{2x}{V}$ mol

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

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

$$K_c = \frac{4x^2}{V^{\cancel{2}}} \times \frac{\cancel{V}}{a-x}$$

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

(2) Chemical method:-

→ amount of reactant or product is determined by suitable chemical reaction, which may be titration in which an indicator is used.

e.g;

→ Consider formation of ethyl acetate by reaction of acitic acid with ethanol.

→ The amount of acetic acid used is determined by titrating it with standard solution of NaOH using phenolphthaline as an indicator.

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

$t=0$	a mole	b mole	zero	zero
$t=t_{eq}$	$\frac{a-x}{V}$	$\frac{b-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

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

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

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

- **Synthesis of ammonia:**

$$\underset{(g)}{N_2} + \underset{(g)}{3H_2} \rightleftharpoons \underset{(g)}{2NH_3}$$

	N_2	$3H_2$	$2NH_3$
$t=0$	a	b	zero
$t=t_{eq}$	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

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

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

$$K_c = \frac{4x^2}{\cancel{V^2}} \times \frac{V}{a-x} \times \frac{V^{\cancel{3}}}{(b-3x)^3}$$

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

- **Preparation of Sulphur trioxide:**

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

	$2SO_2$	O_2	$2SO_3$
$t=0$	a	b	zero
$t=t_{eq}$	$\frac{a-2x}{V}$	$\frac{a-x}{V}$	$\frac{2x}{V}$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

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

$$K_c = \frac{4x^2}{\cancel{V^2}} \times \frac{\cancel{V^2}}{(a-2x)^2} \times \frac{V}{b-x}$$

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

Application Of Equilibrium Constant

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Equilibrium constant for a reaction can be used to predict;

(i) Direction of reaction
(ii) Extent of reaction
(iii) Effect of various factors on equilibrium position.

① Direction of reaction

Direction of reaction can be predicted when magnitude of K_c and reaction quotient (Q) are given.

Reaction Quotient:

"Reaction quotient (Q) is defined as ratio between concentration of products and reactants at any particular time."

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]}$$

CASES:

There are three cases.

(i) Case I:

If reaction quotient Q is less than K_c, reaction will proceed in forward direction.

(ii) Case II:

If $Q > K_c$, reaction will proceed in backward direction.

(iii) Case III:

If $Q = K_c$, reaction is at equilibrium.

② Extent of reaction

The extent of a reaction can be predicted when magnitude of K_c is given.

CASES:

There are three cases.

(i) Case I:

When K_c is very large, reactant is unstable and product is stable, and reaction is almost completed in forward direction.

e.g:

$$H_{2(g)} + Br_{(g)} \rightleftharpoons 2HBr_{(g)}$$

$K_c = 5.4 \times 10^{18}$ at 25°C.

For concentration of HBr:

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$$K_c = \frac{[HBr]^2}{[H_2][Br]}$$

$$\sqrt{5.4 \times 10^{18}} = \sqrt{\frac{[HBr]^2}{(1)(1)}}$$

2.32×10^{9} M $= HBr$

(ii) Case II:

When K_c is very small, reactant is stable and product is unstable and reaction is almost completed in backward direction.

e.g;

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

$$K_c = 1.0 \times 10^{-30} \text{ at } 25^\circ C$$

For concentration of NO.

$$\sqrt{1.0 \times 10^{-30}} = \sqrt{\frac{[NO]^2}{(1)(1)}}$$

$$1.5 \times 10^{-15} M = NO$$

So, it can be seen that product (NO) is very less in amount.

(iii) Case III:

When K_c is neither very large nor very small, reactant and product both are stable. Therefore, reaction produce optimum amount of reactant and product at equilibrium.

e.g;

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

$$K_c = 0.36 \text{ at } 25^\circ C$$

$$\sqrt{0.36} = \sqrt{\frac{[NO_2]^2}{(1)}}$$

$$0.6M = NO_2$$

3. Effect of various factors on equilibrium position. (le Chatelier's principle)

The equilibrium position is effected by

(i) Change in concentration

(ii) Change in pressure

(iii) Change in temperature

(iv) Addition of catalyst.

(i) Change in Concentration.

At reactant side:

→ When reactant's concentration is increased, reaction will proceed in forward direction, shifting equilibrium towards product.

→ When reactant's concentration is decreased, reaction will move in backward direction, shifting equilibrium towards reactants.

At product side:

→ Addition of product increases rate of backward reaction, shifting equilibrium towards reactants.

→ Decrease in product increases rate of forward reaction, shifting equilibrium towards product.

Example:

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$

→ Increase in concentration of CO_2 or H_2 and decrease in concentration of CO or H_2O causes equilibrium to shift towards products.

→ Contrary to it, increase in concentration of CO or H_2O at product side and decrease in concentration of CO_2 or H_2 at reactant side causes equilibrium to be shifted towards reactants.

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(ii) Change in pressure and volume.

• **Increase in pressure / Decrease Volume:**

When pressure on a reaction is increased, the reaction will proceed in the direction where number of moles are lesser and equilibrium will be shifted there.

Example:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

As no. of moles are lesser at product side. Therefore, increase in pressure will shift equilibrium towards SO_3 (at product side)

• **Decrease pressure / Increase volume:**

By decreasing pressure, equilibrium is shifted towards direction where no. of moles are greater.

(iii) Change in Temperature.

• **Increase in temperature:**

⇒ When temp. is increased, reaction moves towards the direction where it is endothermic

e.g.)

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad (1) \quad \Delta H = -198\,kJ$$

—ive sign shows that reaction is exothermic, It means that SO_2 reacts with O_2 to form SO_3 with energy released.

When this reaction is reversed as

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)} \quad (2) \quad \Delta H = 198\,J$$

ΔH (+ive) will show that above reaction is endothermic. So, by increasing temp., reaction (2) will proceed in forward direction and equilibrium is shifted towards product side.

• If the reaction is exothermic, equilibrium will be shifted towards left, and reaction rate towards back will increase by increasing temperature.

- If reaction is endothermic, equilibrium will be shifted towards right by increasing temperature and rate of reation in forward direction will increase.

(iv) Addition of catalyst

- Addition of catalyst will not effect equilibrium position but it only will speed up reaction and decreases time to achieve equilibrium state.

INDUSTRIAL APPLICATIONS OF LE CHATLIER'S PRINCIPLE (SYNTHESIS OF NH_3)

The balanced equation for synthesis of ammonia by Haber's process is given as

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H^\circ = -92.46 KJ$$

It can be seen that

(i) Reaction is exothermic
(ii) Number of moles at reactant side is greater than that of product side.

- According to le-Chatelier's principle, maximum yield of ammonia can be obtaind by:

(i) **Low Temperature:**
As reaction is exothermic, so reaction will

will proceed forward at low temperature. The suitable temperature is $\boxed{400°C}$

(ii) High pressure:

No. of moles are less at product side as compared to reactant side. So, high pressure will shift equilibrium towards right. The suitable pressure is $\boxed{200-300\ atm}$

• Optimum condition:

→ Optimum condition for synthesis of ammonia is low temp. and high pressure.

→ At low temp. yield of ammonia is high but rate of reaction is slow and process becomes uneconomical.

→ A catalyst is used to speed up the reaction. Usually a piece of iron with metal oxide is used.

→ The equilibrium mixture is 35% NH_3 by volume at equilibrium stage.

(iii) Continual removal of ammonia:

Continual removal of product increases yield.

→ Amonia is removed by liquifing it at $-33.4°C$ in refregerating coild and is condensed.

→ The liquid ammonia is thus collected.

→ H_2 and N_2 are not condensed at this temp. so reused in the process.

→ If ammonia is continuosly removed and reaction does not reach to equilibrium position. So, it is possible to convert 100% N_2 and H_2 into ammonia.

SOLUBILITY PRODUCT

Product of molar concentration of opposite charge ion in equilibrium with solid state is called solubility product.

Representation:-
It is denoted by **Ksp** (solubility product constant)

Value:
Its value depends upon temperature.

Applicable:
It can be written only for slightly soluble salts.

e.g

$$CaF_{2(s)} \rightleftharpoons Ca^{+2}_{(aq)} + 2F^{-}_{(aq)}$$

$$K_c = \frac{[Ca^{+2}][F^-]^2}{[CaF_2]}$$

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$$K_c[CaF_2] = [Ca^{+2}][F^-]^2$$

$$\boxed{K_{sp} = [Ca^{+2}][F^-]^2}$$

For general reaction:

$$A_m + B_n \rightleftharpoons mA^{+n} + nB^{-m}$$

$$K_{sp} = [A^{+n}]^m [B^{-m}]^n$$

Applications:

(i) When Ksp of the reaction is given, solubility of the reaction can be calculated and vice versa

PRECIPITATION REACTION

Reaction in which two or more than two solutions are mixed together. As a result, insoluble substance is precipitated out. Such reactions are called precipitated reactions.

CASES:

There are three cases:

→ **Case – I:**

If ion product **(Q')** = solubility product constant **(Ksp)**, solution is saturated but precipitation will not occur.

→ **Case-II:**

If **Q' > Ksp**, solution is super saturated and precipitation will occur until **Q' = Ksp.**

→ **Case – III:**

If **Q' < Ksp,** solution will be unsaturated and precipitation will not occur.

→ Q' is noted before equilibrium.
→ Ksp is calculated at equilibrium.

Common Ion Effect

{ Decrease in solubility or ionization of an electrolyte by the addition of another electrolyte having a common ion is called common ion effect. }

Examples:

①

$$NaCl_{(s)} \rightleftharpoons Na^{\oplus}_{(aq)} + \boxed{Cl^{\ominus}_{(aq)}}$$

$$HCl_{(g)} \rightleftharpoons H^{\oplus}_{(aq)} + \boxed{Cl^{\ominus}_{(aq)}}$$

→ HCl is strong electrolyte than NaCl.

→ When HCl is passed through saturated solution of NaCl, NaCl will precipitate out due to common ion effect of $Cl^{\ominus}$.

②

$$HF_{(l)} \rightleftharpoons H^{\oplus}_{(aq)} + \boxed{F^{\ominus}_{(aq)}}$$

$$NaF_{(s)} \rightleftharpoons Na^{\oplus}_{(aq)} + \boxed{F^{-}_{(aq)}}$$

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→ NaF is strong electrolyte than HF, so when it passes through saturated solution of HF, the solubility of HF is suppressed due to common ion effect of $F^{\ominus}$.

Applications:

1. NaCl is obtained from sea water due to common ion effect.
2. Buffer solution is prepared on the basis of common ion effect.
3. Quantitative analysis (salt analysis) is based on common ion effect.

Self Check Exercises :-

7.1

The following equations represent various industrial reactions at equilibrium. Write K_c expression for each of these reactions. Do not forget to balance the equations.

(i) $SO_{2(g)} + O_{2(g)} \rightleftharpoons SO_{3(g)}$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

(ii) $NH_{3(g)} + O_{2(g)} \rightleftharpoons NO_{(g)} + H_2O_{(g)}$

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$$

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

(iii) $CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)}$$

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]}$$

Give balanced equations for following.

(i) $K_c = \dfrac{[CH_3OH]}{[CO][H_2]^2}$

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

(ii) $K_c = \dfrac{[N_2][H_2O]^2}{[NO]^2[H_2]^2}$

$$2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$$

7.2

Determine the units of K_c for following reactions.

(i) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[PCl_3].[Cl_2]}{[PCl_5]}$$

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$$K_c = \frac{\cancel{(mol\ dm^{-3})}(mol\ dm^{-3})}{\cancel{(mol\ dm^{-3})}}$$

$$\boxed{K_c = mol\ dm^{-3}}$$

(ii) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$K_c = \frac{\cancel{(mol\ dm^{-3})^2}}{\cancel{(mol\ dm^{-3})^2}(mol\ dm^{-3})}$$

$$\boxed{K_c = mol^{-1}\ dm^3}$$

(iii) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

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

$$K_c = \frac{\cancel{(mol\ dm^{-3})^2}}{\cancel{(mol\ dm^{-3})}\cancel{(mol\ dm^{-3})}}$$

$$\boxed{K_c = \text{no units}}$$

7.3

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}$$

Calculate K_p if the following concentrations are found at equilibrium.

$[SO_2] = 0.59M$, $[O_2] = 0.05M$ & $[SO_3] = 0.259M$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

$$K_c = \frac{(0.259)^2 (mol\ dm^{-3})^2}{(0.59)^2 (mol\ dm^{-3})^2\ (0.05)(mol\ dm^{-3})}$$

$$K_c = \frac{(0.259)^2}{(0.59)^2 (0.05)} \times \frac{\cancel{(mol\ dm^{-3})^2}}{\cancel{(mol\ dm^{-3})^2}(mol\ dm^{-3})}$$

$$K_c = 3.854\ dm^3\ mol^{-1}$$

As Δn = no. of moles of products − no. of moles of reactants

$= 2 - 3$

$= -1$

T: 298 K

R: 0.0821 $dm^3\ atm\ K^{-1}\ mol^{-1}$

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

$\therefore\ K_p = (3.854)\ dm^3\ mol^{-1} (0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1} \times 298 K)^{-1}$

$K_p = 3.854 (0.0821 \times 298)^{-1}\ \cancel{dm^3}\ \cancel{mol^{-1}} \cdot \cancel{dm^{-3}}\ atm^{-1}\ \cancel{K}\ \cancel{mol}\ \cancel{K^{-1}}$

$K_p = 3.854 (0.0821 \times 298\ atm)^{-1}$

$$K_p = \frac{3.854}{0.0821 \times 298}\ atm$$

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$K_p = 0.1576\ atm$

7.4

Write K_c and K_p expression for followings

(i) $FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$

$$K_c = \frac{[CO_2]}{[CO]}$$

$$K_p = \frac{P_{CO_2}}{P_{CO}}$$

In equilibrium expressions, only gases are considered

(ii) $P_{4(s)} + 5O_{2(g)} \rightleftharpoons P_4O_{10}{(s)}$

$$K_c = \frac{1}{[O_2]^5}$$

$$K_c = \frac{1}{P_{O_2}^5}$$

(iii) $CH_{4(g)} + 4Cl_{2(g)} \rightleftharpoons CCl_{4(l)} + 4HCl_{(g)}$

$$K_c = \frac{[HCl]^4}{[CH_4][Cl_2]^4}$$

$$K_p = \frac{P_{HCl}^4}{P_{CH_4} \times P_{Cl_2}^4}$$

7.5

For the reaction

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

$K_c = 0.60$ at 500°C. If mixture of 0.30M of each H_2 and CO_2 is heated at 500°C, calculate the conc. of CO at equilibrium.

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

Initial Conc.	0.3M	0.3M	Zero	Zero	$t=0$
Equ. Conc.	$(0.3-x)$M	$(0.3-x)$M	x	x	t_{equ}

As, $K_c = \dfrac{[H_2O][CO]}{[H_2][CO_2]}$

Putting values:

$$0.60 = \frac{x \cdot x}{(0.3-x)(0.3-x)}$$

$$\sqrt{0.6} = \sqrt{\frac{x^2}{(0.3-x)^2}}$$

$$0.774 = \frac{\sqrt{x^{\cancel{2}}}}{\sqrt{(0.3-x)^{\cancel{2}}}}$$

$$(0.3-x)0.774 = x$$

$$0.2323 - 0.774x = x$$

$$0.2323 = x + 0.774x$$

$$x(1+0.774) = 0.2323$$

$$x = \frac{0.2323}{(1+0.774)}$$

$$x = \frac{0.2323}{1.774}$$

$$\boxed{x = 0.130}$$

$\therefore$ Conc. of CO at equilibrium is 0.130 moles

7.6

(i) Fructose $\rightleftharpoons$ Glucose

An analyst prepared a 0.25 M fructose solution at room temperature. At equilibrium he found that its concentration decreased by 0.038M. Calculate K_c for the reaction

Solution:

Fructose $\rightleftharpoons$	Glucose	
0.25 M	zero	$t=0$
(0.25 − 0.038)	0.038	t_{equ}
0.212	0.038	

$$K_c = \frac{[Glucose]}{[Fructose]}$$

$$K_c = \frac{0.038\ M}{0.212\ M}$$

$$\boxed{K_c = 0.179}$$

(ii) When 3.88 moles of NO and 0.88 moles of CO_2 were heated in a flask at a certain temperature. At equilibrium 0.11 moles of each of product were present. Calculate K_c for reaction.

Solution:

$$CO_{2(g)} + NO_{(g)} \rightleftharpoons CO_{(g)} + NO_{2(g)}$$

	CO_2	NO	CO	NO_2	
Initial conc.	0.88 moles	3.88 moles	zero	zero moles	
Equ. conc.	(0.88−0.11) = 0.77	(0.88−0.11) 3.77	0.11 0.11	0.11 0.11	t=equ.

$$K_c = \frac{[CO][NO_2]}{[CO_2][NO]}$$

$$K_c = \frac{0.11 \text{ moles} \times 0.11 \text{ moles}}{0.77 \text{ moles} \times 3.77 \text{ moles}} = \boxed{0.0042}$$

7.7

$$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)} \quad K_c = 8.3\times10^{-4} M$$
at 35°C

Predict direction in which system will shift to attain equilibrium when the concentration of species were found to be
$[COCl_2] = 0.5M$ $[CO] = 2.5\times10^{-2} M$ $[Cl_2] : 2.5\times10^{-2}M$

Solution:

Calculating Q: $Q = \frac{[CO][Cl_2]}{[COCl_2]}$

$$Q = \frac{(2.5\times10^{-2})(2.5\times10^{-2})}{(0.5)}$$

$$Q = \frac{0.000625}{0.5}$$

$$Q = 0.00125\,M = \boxed{1.25\times10^{-3}M}$$

As Q is greater than K_c, so reaction will shift in backward direction.

7.8

White phosphorus (P_4) is produced by reaction of phosphorite rock, [$Ca(PO_4)_2$] with coke. When exposed to air it bursts into smoke and fumes and release a large amount of heat. Predict whether K_c for this reaction is large or small.

$$P_{4(g)} + SO_{2(g)} \rightleftharpoons P_4O_{10(g)}$$

Solution:

The value of K_c is very large in this reaction because reaction happens with burst and produce smoke.

7.9

K_c for the following reaction is 1.0×10^{-3} at 230°C

$$2ICl_{(g)} \rightleftharpoons Cl_{2(g)} + I_{2(g)}$$

1.6 moles of ICl, 0.05 moles of I_2 and ~~0.05~~ 0.05 moles of Cl_2 is present in equilibrium mixture in $2dm^3$ container at 230°C. Determine the equilibrium concentrations of I_2, Cl_2 and ICl when equilibrium is removed after removal of one mole of ICl.

Solution:

Removal of one mol of ICl from equilibrium mixture will shift equilibrium in backward direction. Conc. of I_2 and Cl_2 will decrease by x, whereas conc. of ICl will increase by 2x

	$2ICl$	$\rightleftharpoons$ Cl_2	+ I_2
• Initial conc.	$1.6-1=0.6$	0.05	0.05
• Conc. at equ	$0.6+2x$	$0.05-x$	$0.05-x$
	$\frac{0.6+2x}{2}$	$\frac{0.05-x}{2}$	$\frac{0.05-x}{2}$

$$K_c = \frac{[Cl_2][I_2]}{[ICl]^2}$$

$$1.0\times10^{-3} = \frac{\left[\frac{0.05-x}{2}\right]\left[\frac{0.05-x}{2}\right]}{\left[\frac{0.6+2x}{2}\right]^2}$$

$$\sqrt{1.0\times10^{-3}} = \sqrt{\frac{\left[\frac{0.05-x}{2}\right]^2}{\left[\frac{0.6+2x}{2}\right]^2}}$$

$$3.1\times10^{-3} = \frac{0.05-x}{0.6+2x}$$

$$(3.1\times10^{-3})(0.6+2x) = 0.05-x$$

$$x = \frac{0.03104}{1.0622}$$

$x = 0.0292\ mol\,dm^{-3}$

For [ICl]:

$0.6+2x = 0.6 + 2(0.0292)$

$x = 0.6584\ mol\,dm^{-3}$

For $[I_2]$: $0.05-x = 0.05-0.0292$

$= 0.0208\ mol\,dm^{-3}$

For $[Cl_2]$: $0.05-x = 0.05-0.0292$

$= 0.0208\ mol\,dm^{-3}$

7.10

Solution:

∵ The reaction proceeds in direction where no. of moles are high when pressure is ~~incr~~ decreased.

As no. of moles are greater on reactant side so, by decreasing pressure, reaction will proceed in backward direction. Thus, approach of student is unreasonable.

7.11

Effect of temp = ?

Solution:

(i) $$2I_{(g)} \rightleftharpoons I_{2(g)}$$

Formation of bonds give rise to I_2. As bond formation releases energy so, it is exothermic process. Therefore, decrease of temp will shift the reaction in forward direction.

(ii) $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(l)}$ exothermic

As reaction is exothermic, so increase of temp. will shift the reaction in backward direction.

7.12

Solution:

(i)

Ksp:

Iron (II) hydroxide:

(i) $Fe(OH)_2 \rightleftharpoons Fe^{2+}_{(aq)} + 2OH^{-}_{(aq)}$

$$K_{sp} = [Fe^{2+}_{(aq)}][OH^{-1}_{(aq)}]^2$$

Calcium sulphate

$CaSO_4 \rightleftharpoons Ca^{2+} + SO_4^{2-}$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

(ii)

Solubility of Lead (II) sulphate: ?

Ksp : 1.96×10^{-8} at 25°C

$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-}$

$K_{sp} = [Pb^{2+}][SO_4^{2-}]$ $\quad [Pb^{2+}] = S \ mol\,dm^{-3}$

$[SO_4^{2-}] = S \ mol\,dm^{-3}$

$1.96\times10^{-8} = [Pb^{2+}][SO_4^{2-}]$

$1.96\times10^{-8} = S \cdot S \ (mol\,dm^{-3})^2$

$1.96\times10^{-8} = S^2 \ (mol\,dm^{-3})^2$

$1.96\times10^{-8}(mol\,dm^{-3})^2 = S^2$

$\sqrt{1.96\times10^{-8}(mol\,dm^{-3})^2} = \sqrt{S^2}$

$$\boxed{1.4\times10^{-4} mol\,dm^{-3} = S}$$

(iii)

$$Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$$

$$Q' = [Ca^{2+}]^3[PO_4^{3-}]^2$$

&

$$K_{sp} = 1.2\times10^{-29} \text{ at } 25^\circ C$$

As

$$Q' = [Ca^{2+}]^3[PO_4^{3-}]^2$$

By putting values.

$$Q' = (1\times10^{-9})^3(1\times10^{-9})^2 = \boxed{10^{-45}}$$

Q' $\boxed{10^{-45}}$ is much less than K_{sp} $\boxed{1.2\times10^{-29}}$, $\boxed{\text{no precipitation will occur}}$

The End

Exercise Ch#7
CHEMICAL EQUILIBRIUM:-

Q1 MCQ's

(i) (b) (ii) (c) (iii) (c) (iv) (e)
(v) (c) (vi) (b) (vii) (a) (viii) 4(a,d)

Q:2 Define chemical Equilibrium.

Ans. "State at which rate of forward reaction and backward reaction become equal to each other this is called "Chemical Equilibrium State."

OR

State at which concentration of reactants and products become constant is called "Chemical equilibrium State."

E.g: $H_2O + CO \rightleftharpoons CO_2 + H_2$

Q (Extra) State the necessary condition for equilibrium and the ways that equilibrium can be recognized.

Ans **Conditions for Equilibrium:**

Important features of equilibrium constant expression are as follows:

1) Kc applies only at equilibrium. Value of Kc depend upon temperature. Its value increasing with increase in temperature.
2) If Kc of reaction is 1 concentration of reactants and product are equal.
3) If Kc of reaction is greater than 1, concentration of product is greater than concentration of reactants.

4) If Kc of reaction is less than 1 concentration of reactant is greater than concentration of product.

E.g: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

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

Q (Extra) Describe the microscopic events that occur when a chemical system is in equilibrium.

Ans: When a chemical system is in equilibrium the reaction seems to be stopped. But on microscopic level there is a continuous reaction taking place b/w reactants and product. i.e on both sides of reaction, molecules of reactants and product keep colliding with each other but only the rate of forward reaction becomes equal to rate of reverse reaction.

Q3) Define and explain following terms

(i) Reaction quotient:

The ratio of concentration of products to concentration of reactant at any particular time is called "**Reaction Quotient.**"

→ **Representation:-**

It is represented by "**Q**".

→ **Formula:-**

$$Q = \frac{[Product]}{[Reactant]}$$

→ **Explanation:**
The value of reaction quotient is obtained by taking the ratio of concentration of reactants at any instant 't'. It is used to determine or explain the direction of a reaction by comparing its value with the value of equilibrium constant 'K_c'.

ii) **Solubility Product:-**
It is defined as,
"the product of equilibrium concentration of ions, each raised to a power which is the coefficient of the ion in the balanced equation"

→ **Representation:-**
It is represented by "K_{sp}".

→ **Formula (Expression):**

$$A_mB_{n(s)} \rightleftharpoons mA^{+n}(aq) + nB^{-m}(aq)$$

$$K_{sp} = [A^{+n}]^m [B^{-m}]^n$$

Explanation:
The solubility product constant is equal to the product of equilibrium concentration of ions each raised to a power equal to the no. of such ions in the formula unit of the compound.

iii) "Common Ion Effect:"

Decrease in solubility or an ionization of an electrolyte by the addition of an another electrolyte having a common ion is called "Common Ion Effect."

→ **Example:**

When HCl gas is passed through the saturated solution of NaCl, NaCl is precipitated out due to common ion effect. Solubility of NaCl is less as compared to HCl gas in water. Therefore NaCl is precipitated out.

iv) Heterogenous Equilibrium:

Equilibria which involve more than one phases are called "Heterogenous Equilibria".

→ **Example:**

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

$C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2\,(g)}$

(v) Ion Product:-

The product of concentration of apposite charge ion called an "**Ion Product**."

Example:

For example when CaF_2 is mixed with water. Following equilibrium is established.

$$CaF_{2\,(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

Kc for this equilibrium can be written as.

$$K_c = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$$

Since CaF_2 is slightly soluble salt its concentration almost remains constant therefore

$$K_c\,[CaF_2] = [Ca^{2+}][F^-]^2$$

Q:4 Explain industrial application of Le-chatelier principle using Haber's process an example ?

→ **Defination:-**

According to this Le-chatelier's principle, "When stress is applied to the system which is at equilibrium it tries to minimize this effect."

→ **Applications of Le-chatelier's Principle:-**

Synthesis of Ammonia by Haber's Prcoss:-

$$\underset{(g)}{N_2} + \underset{(g)}{3H_2} \underset{400°C}{\overset{200\text{-}300}{\rightleftharpoons}} \underset{(g)}{2NH_3} \qquad \Delta H = -92.46\,K/J$$

1) **Effect of change in concentration:-**

When nitrogen and hydrogen is continuously added and ammonia is continuosly removed reaction will proceed in forward direction.

(ii) **Effect of change in Pressure:-**

According To Le-Chatlier's Principle when pressure is increased on a reaction will proceed in that direction in which no of moles are less when pressure in this reaction will proceed in forward direction no of moles are less, optimum pressure for this realtion is 200-300 atm.

iii **Effect of Change in temperature:**

According to Le-Chatlier's Principle when temperature is increased on a reaction which is at equilibrium reaction will proceed in that direction in which heat is absorbed endothermic. When temperature is increased in this reaction, reaction will proceed in backward direction because in backward direction is endothermic. Therefore formation of NH_3 is favourable at low temperature optimum temperature for this reaction is 400 °C or 673 K.

iv **Effect of catalyst:-**

Substance which increase the rate of reaction without being consumed is called catalyst. It increase rate of reaction with being consumed by decreasing activation energy. There is no effect of catalyst on equilibrium position. However it decreases the equilibrium time for synthesis of ammonia iron pieces are used as a catalyst which are embeded with Al_2O_3, SiO_2, and MgO.

Q:5 **Propose microscopic events that accounts for observed macroscopic Changes that takes place during a shift in equilibrium.**

Microscopic events that occur when the equilibrium is shifted are as follows.

(i) When the collisions of molecules of product increase. The reaction will shift to the reactant side because on the reactant side no of collisions are less.

(ii) When the collisions of molecules of reactants increase due to increase in concentration of reactants, the reaction will move to product side or will shift to the side where collisions of molecules are less.

Q:6 **$50cm^3$ of acetic acid ($d = 1.049 gcm^{-3}$) is mixed with $50cm^3$ of ethanol ($d = 0.789 gcm^{-3}$) What is the equilibrium composition of the mixture at $25^\circ C$ ($K_c = 4$).**

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(a) Mass of CH_3COOH:-

$d = \frac{m}{V}$

$m = V.d$

$m = 50 \times 1.0499$

$m = 52.495 g$

Mole of CH_3COOH

$mole = \frac{52.495}{60}$

$= 0.875$ moles.

(b) Mass of C_2H_5OH:-

$m = d \times V$

$= 0.789 \times 50$

$= 39.45 g$

Mole of $C_2H_5OH = \frac{39.45}{46}$

$= 0.857$ moles

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

0.875	0.857	0	0
$0.875 - x$	$0.857 - x$	x	x

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$4 = \frac{[x][x]}{[0.875-x][0.857-x]}$$

$4(0.874 - x)(0.857 - x) = x^2$

$4(0.749 - 0.874x - 0.857x + x^2) = x^2$

$4(0.749 - 1.731x + x^2) = x^2$

$2.996 - 6.924x + 4x^2 = x^2$

Q.7 Write K_c and K_p expression for following reactions.

(i) $SO_{2(g)} + \frac{1}{2} O_{2(g)} \rightleftharpoons SO_{3(g)}$

$$K_c = \frac{[SO_3]}{[SO_2][O_2]^{1/2}}$$

$$K_p = \frac{P_{SO_3}}{P_{SO_2} \cdot P_{O_2}^{1/2}}$$

(ii) $H_2O_{(g)} + Cl_2O_{(g)} \rightleftharpoons 2HOCl_{(g)}$

$$K_c = \frac{[HOCl]^2}{[H_2O][Cl_2O]}$$

$$K_p = \frac{P_{HOCl}^2}{P_{H_2O} \; P_{Cl_2O}}$$

(iii) $O_{3(g)} \rightleftharpoons O_{2(g)} + O_{(g)}$

$$K_c = \frac{[O_2][O]}{[O_3]}$$

$$K_p = \frac{P_{O_2} \cdot P_O}{P_{O_3}}$$

(iv) $O_{3(g)} \rightleftharpoons \frac{3}{2} O_{2(g)}$

$$K_c = \frac{[O_2]^{3/2}}{[O_3]}$$

$$K_p = \frac{P_{O_2}^{3/2}}{P_{O_3}}$$

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

$$K_c = \frac{[H_2O]}{[H_2]}$$

$K_p = P_{H_2O}$

"

(vi) $2NO_{(g)} + Cl_{2(g)} \rightleftharpoons 2NOCl$

$$K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]}$$

$$K_p = \frac{P^2_{NOCl}}{P^2_{NO} \cdot P_{Cl_2}}$$

(vii) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_2(g)$

$$K_c = [CO_2]$$

$$K_p = P_{CO_2}$$

(viii) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

$$K_p = \frac{P_{CO} \cdot P_{H_2}}{P_{H_2O}}$$

Q Extra $K_c = 2.6 \times 10^{-5}$ at $125°C$ for the reaction

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

Calculate K_p at this temperature.

⇒ Solution:-

$K_c = 2.6 \times 10^{-5}$

$T = 125°C = 398\,K$

$R = 0.0821\,atm\,dm^3\,K^{-1}\,mol^{-1}$

$2NH_3 \rightleftharpoons N_2 + 3H_2$

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

$\Delta n = 4 - 2 = 2$

$K_p = (2.6 \times 10^{-5})(0.0821 \times 398)^2 \Rightarrow \boxed{K_p = 0.028}$

Q:8: At a particular temperature $K_p = 0.133$ atm. Which of the following conditions corresponds to equilibrium position for the reaction.

$$A_{(g)} \rightleftharpoons 2B$$

(a) $P_B = 0.175$ atm, $P_A = 0.102$ atm

$$K_p = \frac{P_B^2}{P_A}$$

$$K_p = \frac{[0.175]^2}{[0.102]}$$

$K_p = 0.300$ atm Which is not equal to 0.133 atm

(b) $P_B = 0.064$ atm, $P_A = 0.0308$ atm

$$K_p = \frac{P_B^2}{P_A}$$

$$K_p = \frac{[0.064]^2}{[0.0308]}$$

$\boxed{K_p = 0.133 \text{ atm which is equal to } 0.133 \text{ atm}}$

(c) $P_B = 0.144$ atm, $P_A = 0.156$ atm

$$K_p = \frac{P_B^2}{P_A}$$

$$K_p = \frac{[0.144]^2}{[0.156]}$$

$\boxed{K_p = 0.133 \text{ atm which is } = 0.133 \text{ atm}}$

Q.9 Write expression for Kc & kp for following process.

(a) Blue vitrol is deep blue solid copper(II)........... sulphate

$$CuSO_4 \cdot 5H_2O_{(s)} \rightleftharpoons CuSO_{4(s)} + 5H_2O_{(g)}$$

$$Kc = [H_2O]^5$$

$$kp = P^5_{H_2O}$$

b) The decomposition of solid phosphorus.......... chlorine gas

$$PCl_{5(s)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

$$Kc = [Cl_2][PCl_3]$$

$$Kp = P_{Cl_2} \cdot P_{PCl_3}$$

Q10 Predict the shift in equilibrium position that will occur for each of the following process when the volume is reduced.

(i) $PCl_{3(g)} + 2NH_{3(g)} \rightleftharpoons P(NH_2)_3(g) + 3HCl(g)$

In this reaction on reducing volume the reaction will move toward left side. i.e backward. Because on decreasing volume reaction moves towards less no of moles.

(ii) $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_2(g)$

On decreasing volume reaction moves towards right side and equilibrium will be shifted to the right side. i.e: in forward direction because on decreasing volume reaction moves towards less no of moles.

(iii) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

On reducing volume reaction will move towards left and equilibrium will be Shifted in the direction of reaction. i.e: in backward direction.

Q11: For each of the following reactions, predict how the value of K_c changes as the 'T' increased

@ $N_2(g) + O_2(g) \rightleftharpoons 2NO \quad \Delta H = 180\,kJ$

As the temperature increased reaction will move in forward direction because given reaction is endothermic and heat is absorbed by reactants. So on increasing temperature more product will be formed as reaction will move towards right.

(b) $2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H^o = -198\,kJ$

The given reaction is exothermic. So, as heat is released in this reaction and it is the point of the product. So on increasing the temperature, reaction will move backward and less product will form.

(c) $N_2O_4 \rightleftharpoons 2NO_2 \quad \Delta H^o = 58\,kJ$

As the given reaction is endothermic Heat will be absorbed by reactants and when the temperature is increased reaction will move towards forward direction i.e: towards product side and on increasing heat, more product will be formed.

(d) $$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3H_{2(g)} \quad \Delta H^\circ = 206\,kJ$$

The given reaction is also endothermic and heat will be absorbed by reactants. Therefore on increasing heat more product will be formed. Reaction will move towards forward direction. i.e:- towards product side (right side).

Q12. **What is difference b/w an equilibrium with a Kc value larger than one compared with an equilibrium that has a Kc smaller one.**

An equilibrium with a greater than one shows that it has greater concentration of products than the concentration of reactants. As by the formula

$$K_c = \frac{[Product]}{[Reactants]}$$

Whereas an equilibrium with a Kc smaller than one shows that reaction has a greater concentration of that of Reactant than product

Q13:- **Describe the behaviour of the following equilibrium with the stated changes.**

a) increasing pressure on

$$C_3H_{8(g)} + 5O_{2(g)} \rightleftharpoons 3CO_{2(g)} + 4H_2O_{(g)}$$

When the pressure is increased on a given reaction, volume will be reduced and reaction will move in backward direction. This is because on increasing pressure reaction will moves towards the side which has less no. of moles as in the given reaction left side in the reaction has less no. of moles.

(b) **Adding $I_2\,(g)$ to $2HI \rightleftharpoons I_2(g) + H_2(g)$**

When we will increase the concentration of iodine, reaction will move in backward direction as concentration of product and no. of collisions of molecules at product increase. So the reaction will move in backward direction.

(c) **Removing heat from:**

$CO_{2\,(g)} \rightleftharpoons CO + \frac{1}{2} O_2\,(g) \quad \Delta H = 284 kJ$

The given reaction is endothermic and heat is absorbed by reactants to give products, So on decreasing heat of reaction less product will be formed and reaction will move in backward direction.

d) **Decreasing pressure on**

$C_2H_6\,(g) \rightleftharpoons H_{2\,(g)} + C_2H_{4\,(g)}$

When pressure will be decreased on the given reaction, volume will increase and reaction will in the direction which has greater no of moles. So, in the given reaction reaction will move towards forward direction i.e: toward the direction of product.

Q14. A solution is prepared by mixing 50 cm^3 of 5×10^{-3} M NaCl with 50cm^3 of 2×10^{-2} M $Pb(NO_3)_2$. Will a precipitate of $PbCl_2$ form? Ksp for $PbCl_2$ is 1.7×10^{-5}.

Total volume of reaction :-

$$50\,cm^3 + 50\,cm^3 = 100\,cm^3$$

$$NaCl \rightarrow Na^+ + Cl^-$$

$$5\times10^{-3} \quad 5\times10^{-3} \quad 5\times10^{-3}$$

Volume of NaCl = 0.05 dm^3

$$[Cl^-] = \frac{[5\times10^{-3}]\times 0.05\,dm^3}{0.1\,dm^3}$$

$$[Cl^-] = 2.5\times10^{-3}\,M$$

$$Pb(NO_3)_2 \rightleftharpoons Pb^{+2} + 2NO_3^{-1}$$

$$2\times10^{-2} \quad 2\times10^{-2} \quad 2\times2\times10^{-2}$$

$$[Pb^{+2}] = \frac{0.05\,dm^3 \times 2\times10^{-2}}{0.1\,dm^3}$$

$$[Pb^{+2}] = 0.01M$$

$$PbCl_2 \rightarrow Pb^{+2} + 2Cl^-$$

$$Q' = [Pb^{+2}][Cl^-]^2$$

$$Q' = [0.01][2.5\times10^{-3}M]^2$$

$$Q' = 6.25\times10^{-8}$$

Whereas,

$$K_{sp}' = 1.7 \times 10^{-5}$$

As $Q' < K_{sp}$, so precipitate will not occur.

Q15 When a solid $PbCl_2$ is added to pure water at 25°C, the salt dissolves until the concentration of Pb^{+2} reaches 1.6×10^{-2} M. After this concentration is reached, excess solid remains undissolved. What is Ksp for this salt.

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$$

$$1.6 \times 10^{-2} \quad 2 \times 1.6 \times 10^{-2}$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = [1.6 \times 10^{-2}][2 \times 1.6 \times 10^{-2}]^2$$

$$K_{sp} = 1.6384 \times 10^{-5}$$

Q (Extra) The equilibrium constant for the following reaction is 1.6×10^5 at 1000K

$$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)}$$

Find the equilibrium pressures of all the gases if 10.0 atm of HBr is introduced into a sealed container at 1000K.

$$K_p = 1.6 \times 10^5 \text{ at } 1000K$$

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

$$x \quad x \quad 10 - 2x$$

$$[HBr] = 10 atm$$

(Question is removed from latest edition of book.)

Q.16 Consider the following gas phase reaction

$SO_{2(g)} + Cl_{2(g)} \rightleftharpoons SO_2Cl_{2(g)} + Heat$

Describe four changes that would drive the equilibrium to left.

Following are the changes that will decieve reaction to the left.

→ (i) when the pressure is decreased reaction will move towards left as no of moles are less on left side.

→ (ii) Reaction will move to left when concentration of SO_2 is decreased.

→ (iii) Reaction will move to left when concentration of Cl_2 will be decreased.

→ (iv) Reaction will move to left when concentration of SO_2Cl_2 will be increased.

→ (v) By increasing temperature reaction will move towards left because the reaction is exothermic.

Q.17- How would you change the volume of following reactions to increase the yield of products.

(i) $Cl_{2(g)} + I_{2(g)} \rightleftharpoons 2ICl$

We will get the more yield from the concentration of Cl_2 and I_2 will be increased. This is because when concentration will be increased collisions of molecules of reactants increase which cause the system to move in forward direction.

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

When the concentration of $2NO_2$ will be increased, reaction will move to right and more yield will be produced

Q 18: A figurine device is used to predict wheather condition is blue on dry, sunny days, and pink on damp, rainy days. These figurines are coated with substances containing chemical species that undergo following equilibrium

$$2[CO(H_2O)_6]^{+2} + 4Cl^- \rightleftharpoons Co[CoCl_4]^{-2} + 12H_2O$$

→ a) Identify the blue substance.

At dry day water will evaporate and reaction will move forward hence blue substance is $\boxed{Co[COCl_4]^{-2}}$

→ b) Identify the pink substance.

On rainy day water vapours increases so the reaction will move backward hence pink substance is $[CO[H_2O)_6]^{+2}$.

(C) How is the Le-Chatlier's Principle applied here?
If we increase concentration of reactant by adding more reactant reaction will proceed in forward direction. If we increase pressure the reaction will proceed in backward direction as number of moles are less. If we increase temperature the reaction will proceed in that direction where it is endothermic. Catalyst increase the rate of reaction by decreasing activation energy. There is no effect of catalyst on equilibrium but it decrease the equilibrium time.

Q Extra The combination of oxygen with hemoglobin(Hb) molecule, which carries oxygen through the blood, is a complex reaction. Four our purpose it can be represented by the simplified equation.

$$Hb_{(aq)} + O_{2(aq)} \rightleftharpoons HbO_{2(aq)}$$

Where HbO_2 is oxyhemoglobin that actually transport oxygen to tissues. The equilibrium constant expression is

$$K_c = \frac{[HbO_2]}{[Hb][O_2]}$$

Haemoglobin: HbO_2 is the mixture of O_2 and Hb. On scaling (climbing) mountain, the concentration of O_2 in the air decreases. Due to this we cannot get sufficient amount of oxygen. As hemoglobin (Hb) molecules carries oxygen through the blood which is important for our body to transport oxygen to tissues. At sea level, the Hb in our body take oxygen from air, the equilibrium b/w air and O_2 disturbs and reaction moves in backward direction. Due to this disturbance Disease like headaches, nausea and vomiting occured.

Q Extra: Baking soda undergoes thermal decomposition as follows.

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + CO_2 + H_2O$$

would we obtain more CO_2 by adding extra baking soda to the reaction mixture.

(a) a closed vessel.

By adding extra amount of baking soda in the reaction, the reaction will proceed in forward direction and CO_2 will be produce. As the reaction takes place in a closed vessel, the equilibrium will establish soon, and we get carbon-dioxide untill equilibrium is established.

(b) An open vessel:-

By adding extra amount of baking soda in the reaction which takes place in an open vessel, the reaction will more in forward direction. As it is in an open vessel. The Carbon dioxide (CO_2) gas releases continuously so we get more amount of CO_2 in an open vessel as compared to the system which is held in a closed vessel.

Q.19: Potassium dichromate solution has beautiful clear orange colour. This is due to the colour of dichromate ion $Cr_2O_7^{+2}$. When a salt is dissolved in water. The following equilibrium is setup. On heating solution.

$$Cr_2O_7^{-2} + H_2O \rightleftharpoons 2CrO_4^{-2} + 2H$$

What will happen?

@ dilute solution hydroxide is added to this solution.

As we are increasing temperature of the reaction the reaction will proceed in that direction where heat is absorbed. i.e:

endothermic when we add dilute sodium hydroxide (NaOH) to the reaction the reaction will proceed in forward direction because sodium hydroxide, is diluted that is quantity of water is larger so the concentration of H_2O increases in the reaction and it will proceed in forward direction.

Q. (Extra) If 0.350 moles of SO_3 is placed in a 1.00 dm^3 flask and allowed to come to equilibrium at high temperature. 0.207 mole of SO_2 remains. Calculate Kc for this reaction.

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$

	(g)	(g)	(g)
t=0	0.350	0	0
t=eq	0.350 − 2x	2x	x
	$\frac{0.350-2x}{1.00}$	$\frac{2x}{1.00}$	$\frac{x}{1.00}$
	0.207	0	0

$0.350 - 2x = .207$

$2x = 0.350 - .207$

$x = \frac{0.143}{2} \rightarrow 0.0715$ putting 'x' value

$$2SO_3 \rightarrow 2SO_2 + O_2$$

$.350 - 2(0.0175)$ $\quad 2(.0175)$ $\quad .0715$

$$K_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$$

$$Kc = \frac{[2 \times 0.0715]^2 [.0715]}{[350 - 2(0.0715)]}$$

$$Kc = \frac{(.02045)(.0715)}{(.04285)}$$

$$Kc = \frac{1.462175 \times 10^{-03}}{0.04285}$$

$$\boxed{Kc = 0.03412}$$

Q20: For this reaction between hydrogen & iodine to form hydrogen Iodide, the value of Kc is 794 at 298 K but 54 at 700K what can you deduce from this information?

On increasing temperature the value of Kc is decreasing this shows that the reaction is exothermic.

$$H_2 + I_2 \rightleftharpoons 2HI + heat$$

According to Le-Chatlier's Principle on increasing temperature, the reaction which is at equilibrium moves in that direction where heat is absorbed. i.e:- Endothermic. Therefore the following reaction proceed in backward direction.

This also shows that we can get more amount of products at this low temperature.

$$Kc = \frac{[Product]}{[Reactent]}$$

$Kc = 794$ at $25°C$ or $298K$

$Kc = 54$ at $427°C$ or $700K$

→ **Conclusions:-**

we can get more amount of products at low temperature.

END!