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Class 11
Chemistry

Chapter 8
Chemical Equilibrium
Handwritten Notes

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Chapter no 08

Chemical Equilibrium

Irreversible and Reversible reactions

- **Irreversible reactions:**

defination: The reactions in which reactants are completely consumed and converted into products are called irreversible reactions.

- These reactions almost go to completion.
- These reactions stop when limiting reactant is used up.
- These reactions are unidirectional.

Example

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

- **Reversible reactions:**

defination: The reactions in which reactants are not completely consumed and are not converted into products are called reversible reactions.

- These reactions never go to completion
- These reactions stop product formation before the compelete consumption of limiting reactants
- These reactions are bidirectional

Example:

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

Microscopic and Macroscopic events

- **Macroscopic events:**
It refers to the phenomena that can be observed with naked eye.
Examples:
  - A change in - colour
  - The evolution or absorption of heat
  - The formation of precipitation

- **Microscopic events:**
It refers to the phenomena that can't be observed with naked eye.
Examples:
  - Collisions between molecules
  - Loss or gain of electrons etc
  - Rearrangement of atoms in molecules.

Reversible reaction & Dynamic Equilibri

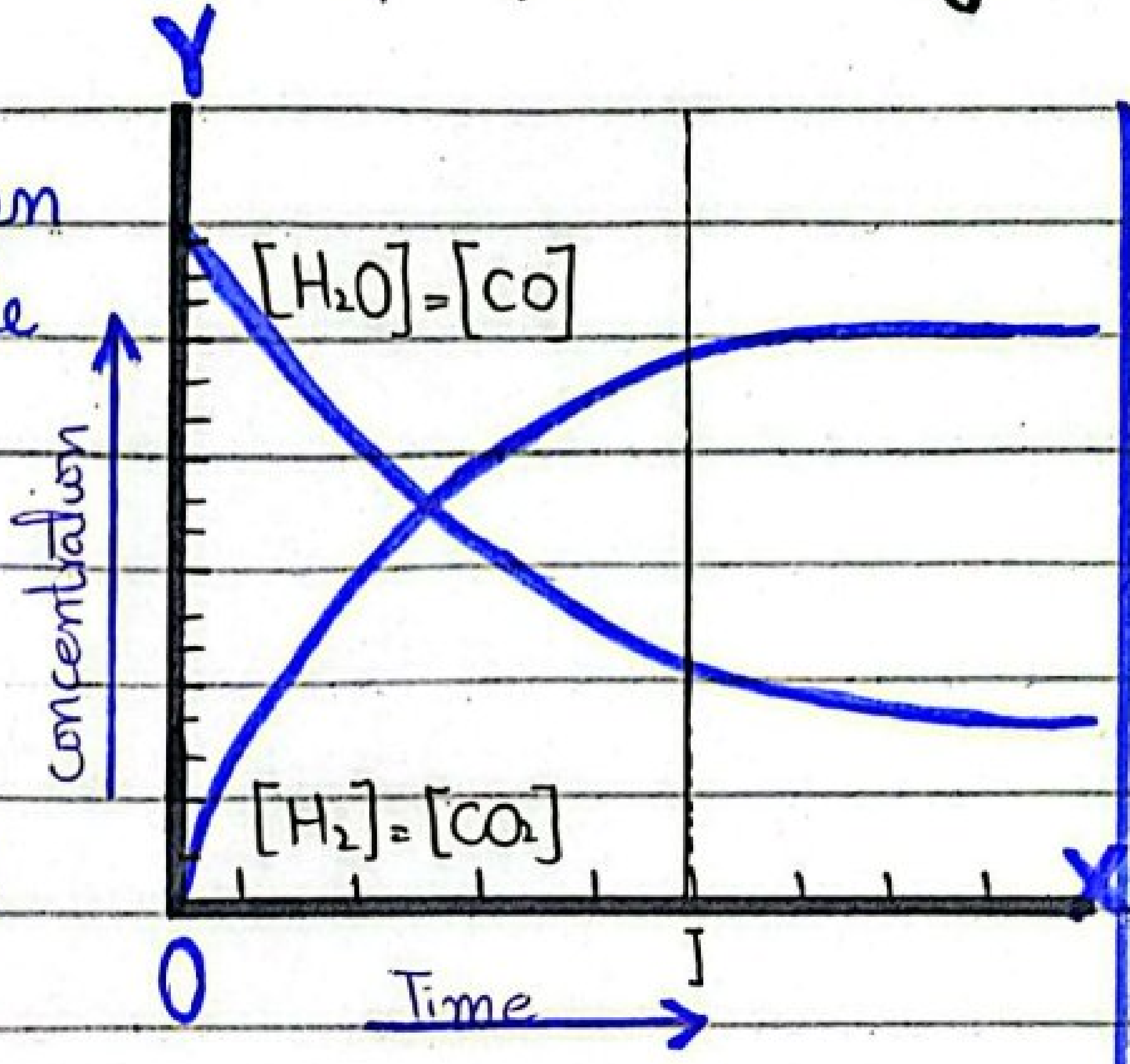
"The state of a reversible reaction at which composition of the reaction mixture does not change is called the state of chemical equilibrium."

It is also called Dynamic equilibrium because

- The concentration of reactants and products become constant
- Rate of forward and reverse reaction is at same speed.
- The equilibrium stage is not affected by time

Explanation

Consider the reaction between steam and Carbonmonoxide



- **Forward reaction:**
initially there are maximum number of collision per second between molecules of CO and H_2O so rate of forward reaction is fast.

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

Slowly, the concentration of reactants decreases.

- **Reverse reaction:**
As reactants are converted into products forward reaction slow down and reverse reaction begins. The products reacts to form reactants

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

- **Chemical equilibrium:**
When both reaction occurs at same speed then the reaction at this stage is said to be in chemical equilibrium

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

The Law of Mass Action

Two chemist **C.M Gulberg** and **P.Wage** in **1864** proposed the law of mass action as a general description of equilibrium state.

It states that
"The rate of chemical reaction is directly proportional to the product of molar concentration of reactants raised to a power equal to its stoichiometric co-efficient in the balanced chemical equation."

OR

" The rate at which a substance reacts is directly proportional to its active mass and chemical reaction rate is proportional to product of active masses of reacting substances

Active mass: The term means the concentration of reactants and products in **moles dm^{-3}** for a dilute solution

Derivation of K_c Expression:

Considering following general reaction

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

where,

A, B, C & D represents chemical species

a, b, c & d are their co-efficients in balanced equation

According to law of mass action

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

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

k_f is rate constant for forward reaction

Rate of reverse reaction, $R_r \propto [C]^c [D]^d$

$= k_r [C]^c [D]^d$

k_r is rate constant for reverse reaction

At equilibrium state

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Rate of forward reaction = Rate of reverse reaction

Thus

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

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

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

where $Kc = k_f/k_r$ is known as equilibrium constant.

The given equation is equilibrium constant expression. which can be written from balanced chemical equation.

Conditions for Equilibrium

Dependence: The value of kc is independent of initial concentration reactant and product but depends upon temperature. !

- It has only one value at a given temperature.

Applicability: kc is only applicable at chemical equilibrium.

Iindication: The subscript 'c' indicates concentration of reactants and products in mole dm^{-3}

Value of kc: It is measured at a given temperature if values of concentration of reactant and products are known.

Magnitude: Magnitude of kc indicates equilibrium's position

- When $k_c < 1$ then concentration of reactant is greater then product.
- When $k_c > 1$ then numerator is greater then denominator reactant's concentration is less then product.

- When $k_c = 1$ then may be concentration is equal.
  k_c expression is written from balanced equation in which products are placed in numerator and reactants in denominator.

Concept Assessment Ex 8.1

1. Write k_c and also 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) $NH_{3(g)} + O_{2(g)} \rightleftharpoons NO_{(g)} + H_2O$

$$4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O$$

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

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

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

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

2- Write equations

$$k_c = \frac{[CH_3OH]}{[CO][H_2]^2} \qquad CO + 2H_2 \rightleftharpoons CH_3OH$$

$$k_c = \frac{[N_2][H_2O]^2}{[NO_2]^2[H_2]^2} \qquad 2NO + 2H_2 \rightleftharpoons N_2 + 2H_2O$$

Concept Assessment Ex 8.2

1- $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 450°C

Calculate kp if $[SO_2] = 0.59M$, $[O_2] = 0.05M$, $[SO_3] = 0.259M$

kc for this equation is

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

$$k_c = \frac{[0.259]^2}{(0.59)^2(0.05)} = \frac{0.067}{0.3481 \times 0.05}$$

$$k_c = 3.85 \approx 4$$

for kp

$$k_p = k_c(RT)^{\Delta n} \qquad \text{ie } R = 0.0821$$

$$k_p = 3.85(0.0821 \times 723)^{-1} \qquad T = 450°C + 273$$

$$k_p = 3.85(59.35)^{-1} \qquad = 723k$$

$$k_p = 3.85(0.0168) \qquad \Delta n = 2 - (2+1)$$

$$k_p = 0.064 \text{ atm} \qquad = -1$$

$$k_c = 3.85$$

Types of Equilibrium

Homogeneous Equilibria:

An equilibrium system in which all of the reactants and products are in the same phase

Examples:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ all gases

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Equilibrium expression:

This equilibrium constant expression includes all reactants and products.

Phase uniformity: It is uniform through out single phase.

Heterogeneous Equilibria:

An equilibrium system in which all of the reactants and products are not in the same phase

Examples:

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

Equilibrium expression:

The equilibrium constant expression doesn't includes pure solids and liquids.

Reason.

If pure solids or pure liquids are involved in an equilibrium system, their concentration are not written in the equilibrium constant expression because change in concentrations of any pure solid or

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liquid has no effect on the equilibrium system.

Concept Assessment Ex 8.3

Write kc and kp expression

1. $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

$$K_c = \frac{[CO_2]}{[CO]} \quad \text{and} \quad K_p = \frac{P_{CO_2}}{P_{CO}}$$

2. $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

$$K_c = [1/[O_2]]^5 \quad \text{and} \quad K_p = \frac{1}{PO_2^5}$$

3. $CH_4(g) + 4Cl_2(g) \rightleftharpoons CCl_4(l) + 4HCl(g)$

$$K_c = \frac{[HCl]^4}{[Cl_2]^4[CH_4]} \quad \text{and} \quad K_p = \frac{P_{HCl}^4}{P_{Cl_2}^4 \times P_{CH_4}}$$

Ways to recoganize equilibrium

Equilibrium constant expression can be determined by physical as well as chemical methods.

- **Physical Method**

In this method, a physical property of the reaction mixture is determined during the uprogress of reaction.

- The widely measured property is absorption of radiation

Spectrometric Method: This method is used when

a reactant or a product absorbes ultraviolet or infrared radiations.
Concentration of reactants and products is determined by the amount of radiations absorbed.

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

(Colourless) (Reddish brown)

Progress is studied by measuring absorpance at regular intervals that is directly related to NO_2's concentration

- At equilibrium spectropotometer will show constant value of absorbance.

Chemical Method

In this method the amount of reactant or product is determined by suitable chemical reaction.

For example:

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

acetic acid + ethanol ⇌ ethyl acetate + water

Mineral acid is added in the reaction to catalyze it.
Progress is studied by determining concentration of acetic acid, by titrating it against solution of NaOH using Phenolphthalein as an indicator.
Till equilibrium is attained acetic acid's concentration decreases and at equilibrium it's concentration remains constant.

The Le Chatelier's Principle

It states that:

"if a change is imposed on a system at equilibrium the position of the equilibrium will shift in a direction which tends to reduce that change."

factors affecting Equilibrium

According to Le chateliers principle the factors that affect equilibrium are:

1 The Effect of Change in Concentration:

According to the principle of Le chatelier, the equilibrium shifts to accomodate the substance added or removed and restore equilibrium again.

• When concentration of one or more reactant or product is disturbed, the system will not remain in equilibrium state.

For example:

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

1) Reactants are added:-

When reactants like CO_2 and H_2 are added, the reaction will proceed in forward direction. They react to give CO and H_2O

2) Reactants are removed:-

When reactants like CO_2 and H_2 are removed, the reaction will proceed in reverse/backward direction. Products CO and H_2O react to given CO_2 and H_2.

3) Products are added:-

When products $(CO + H_2O)$ are added, reaction will proceed in reverse direction. CO and H_2O react to give reactants. Higher concentration → lower

4) Products are removed:

When products are removed, then the reaction proceed in forward direction, because concentration of reactants is high.

Equilibrium establishment:-

Wether the reaction will proceed in the forward or reverse reaction the concentration of reactants and products must become constant and equilibrium would establish.

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2. The Effect of Change in Pressure:

When pressure of a system at equilibrium is increased then the reaction will proceed in the direction having smaller number of gaseous molecules in the balanced chemical equation.

For example:

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

1) Pressure increases:

When pressure is increased the reaction proceed in forward direction because it has the lower number of gaseous molecules.

2) Pressure decreases:

When pressure is decreased then the reaction proceed in reverse reaction towards left. (towards higher concentration)

3 The Effect of Change in Volume

When volume of a system at equilibrium is increased reaction will proceed in the direction having higher number of gaseous molecules in the balanced chemical equation.

$$\text{Volume} \propto n$$

For example:

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

1) Volume increases:

When volume increases the reaction will proceeded towards left, backward direction, where the number of molecules is high.

2) Volume decreases:

If volume decreases the reaction will proceeded in the direction where no. of molecules is low towards right.

Volume-Pressure relationship: Both are indirectly related if Increase in pressure brings reaction towards right but increase in volume brings it towards left.

Applicability of P & V to affect equilibrium

Changes in pressure and volume can only affect equilibrium when;

- All reacting molecules and products have same gaseous state
- When molar concentration of products and reactants is different.

Pressure and volume doesn't affect under following cases:

Case no 1

Pressure and volume doesn't effect when no of moles of Product and reactant is equal.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad 2\text{ moles} \rightleftharpoons 2\text{ moles}.$$

Case no 2

There is no effect of pressure and volume in case of solid and liquid state.

$$P_4(s) + 5O(g) \rightleftharpoons P_4O_{10}(s)$$

54 ## The Effect of Change in Temperature

Temperature affects endothermic and exothermic reaction differently.

In case of Endothermic reaction, increase in temperature brings the reaction towards forward direction

In case of Exothermic reaction, increase in temperature proceeds the reaction in backward direction

Exothermic reaction

$$2SO_2\,g + O_2\,g \rightleftharpoons 2SO_3(g) + \text{heat}$$

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

Increase in temperature proceeds it backward so for exothemic reactions decrease in temperature is favourable.

$$kc = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \begin{array}{l} \leftarrow \text{decrease} \\ \leftarrow \text{Increase} \end{array}$$

$kc = 2.8 \times 10^2$ at 1000 k
$kc = 29 \times 10^{26}$ at 298 k

that's why production of SO_3 is favoured at low temperature.

Endothermic reaction:

$$N_2O_{4g} \rightleftharpoons 2NO_{2(g)} \quad \Delta H^\circ = +57.2$$

or $$N_2O_{4(g)} + \text{Heat} \rightleftharpoons 2NO_{2\,(g)}$$

Increase in temperature proceeds reaction toward right

$$k = \frac{[NO_2]^2}{[N_2O_4]} \begin{array}{l} \leftarrow \text{increase} \\ \leftarrow \text{decrease} \end{array}$$

$kc = 7.7 \times 10^{-5}$ at $0^\circ C$
$kc = 0.4$ at $100^\circ C$

So, high temperatures favours NO_2 production.

5. The Effect of Addition of Catalyst

Catalyst: Substance that increase the rate of reaction without being consumed is called catalyst.

- When it is added it speeds up both forward and reverse reaction at same degree.
- It decreases the time to reach equilibrium
- It doesnot affect when reaction is at equilibrium position.

Example:

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

Concept Assessment Ex 8.4

1. $k_c = 1.0 \times 10^{-3}$ at 230°C for

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

if $I_2 = Cl_2 = 0.05$ and $ICl = 1.6$ moles. Determine the equilibrium concentrations of I_2, Cl_2 & ICl after removal of one mole of ICl.

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

$$1.6 - 1 = 0.6 \qquad 0.05 \qquad 0.05$$

Conc. at new equilibrium $\quad 0.6 + 2x \qquad 0.05 - x \qquad 0.05 - x$

In moles dm^{-3} $\quad \frac{0.6+2x}{2} \qquad \frac{0.05-x}{2} \qquad \frac{0.05-x}{2}$

$$k_c = \frac{[Cl_2][I_2]}{[ICl]^2} \Rightarrow \frac{\left[\frac{0.05-x}{2}\right]\left[\frac{0.05-x}{2}\right]}{\left[\frac{0.6+2x}{2}\right]^2}$$

$$1.0 \times 10^{-3} = \frac{\left[0.05 - x/2\right]^2}{\left[\frac{0.6+2x}{2}\right]^2}$$

taking $\sqrt{\ }$ on B.S

$$\sqrt{1.0 \times 10^{-3}} = \sqrt{\frac{(0.05 - x/2)^2}{(0.6 - 2x/2)^2}}$$

$$0.03162 = \frac{0.05 - x}{0.06 - 2x}$$

$$0.03162(0.06 - 2x) = 0.05 - x$$

$$0.018 - 0.063x = 0.05 - x$$

$$0.018 - 0.05 = -x - 0.063x$$

$$-0.0310 = -1.0632x$$

$$x = \frac{-0.0310}{-1.063}$$

$$x = 0.029$$

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$[ICl] = 0.6 + 2x$

$= 0.6 + 2 \times 0.029 \Rightarrow \underline{0.658M}$

$[I_2] = [Cl_2] = 0.05 - x$

$= 0.05 - 0.029$

$= \underline{0.021M}$

Concept Assessment Ex 8.5

1 $$CO_g + 2H_{2g} \rightleftharpoons CH_3OH_g$$

decrease in pressure over the system increases product yeild?

The no. of molecules of reactants are 3 while product is 1 so decrease in pressure causes the reaction to shift towards higher concentration ie towards left. So to increase yeild it is wrong. Yeild can be increased if pressure is increases.

Concept Assessment Ex 8.6

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

1- What's effect does decrease in temperature imposes?

$$2I_g \rightleftharpoons I_{2(g)} + \text{heat}$$

It is an exothermic reaction so for such a reaction decrease in temperatures cause it to proceed in the forward direction. so concencentration of I decreases because it forms I_2

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

2- Predict the effect of increase in temperature on product?

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} + heat$$

According to Le chateliers principle for an enother-mic reaction increase in temperature proceeds it in reverse / backward direction. So, increase in temperature causes lower yeild of product. (CH_3OH)

Industrial Applications of LeChatelier's principle

For industrial process it is important to maximize the concentration of product and minimize the leftover reactants.

Synthesis of Ammonia by Haber's Process

The reaction involved in formation of Ammonia is

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad \Delta H = -92.46$$

- The reaction is exothermic.
- The reaction proceeds with decrease in no. of moles.

Le chatelier principle suggests three ways to get maximum yeild.

Low Temperature:

The reaction is exothermic therefore, low temperature will favour the formation of ammonia.

- The suitable temperature is 400°C

High Pressure

high pressure shifts the reaction towards lower molar concentration i.e towards right. (formation of ammonia)

- The most suitable pressure is 200-300 atm

Optimum Condition

The optimum Condition for equilibrium production of ammonia is low temperature and high pressure.

Draw backs

- Beyond a limit, temperature decrease, still production of NH_3 is high but the process becomes uneconomical because rate of formation is slow, it'ill take more time and Labour cost.
- If the pressure is too high, it causes the gases to liquify thus we can't increase it, upto a limit.

Addition of Catalyst

A catalyst is used to overcome the drawbacks and to increase the rate of reaction.

- A piece of iron Fe and other metal oxides MgO, SiO_2, Al_2O_3 are used.

Continual removal of NH_3

According to Le chatlier principle if the product is removed continuously then equilibrium is shift towards the right side. Continuously removing of NH_3 greatly increases the production of ammonia.

Method to remove ammonia:

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Ammonia is liquefied by cooling it through a refrigerator until it condenses at $-33.4^\circ C$ and then removed. N_2 & H_2 don't condence at this temperature and are recycled.

- Stree caused by removal of ammonia doesn't allow reaction to reach equilibrium by shifting reaction towards right.

- The equilibrium mixture contain 35% NH_3 by Volume.
- 100% converion of H_2 and N_2 to NH_3 is possible.

Synthesis of Sulphuric Acid by Contact Process

The contact process in industries is used to produce sulphuric acid. It involves following chemical reactions.

Formation of Sulphur dioxide

Firstly, sulphur dioxide is produced by burning process.

$$S_{(s)} + O_{2(g)} \longrightarrow SO_{2(g)}$$

Oxidation of SO_2

SO_2 is oxidized into SO_3 by using Varadium penta oxide (V_2O_5).

$$2SO_{2(g)} + O_2 g \xrightleftharpoons{V_2O_5} 2SO_{3(g)} \quad \Delta H = -198 kJ$$

Conversion of sulphur dioxide to sulphur trioxide is the most important process inthe production of sulphoric acid.

- The reaction is exothermic.
- The reaction occurs with a decrease in no. of moles.

Le chatelier principle suggests three ways to maximize yeild.

Low Temperature

The reaction is exothermic so low temperature proceeds the reaction toward right i.e production of suphuric acid.
The temperature that is suitable is **400-500°C**

High Pressure

As forward reaction proceeds fewer moles so high pressure shift the reaction in forward direction
The compromized pressure of **2atm** is used

Adding excess oxygen

- Increase in O_2 favours product formation.
- Adding too much O_2 decreases the reaction rate and product formation.

Ratio:
A degraded **1:1** ratio of SO_2 & O_2 is used to obtain high yields.

Exercise

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1.	(b) pressure	2.	(b) $A_g \rightleftharpoons B_{(g)}$	3.	(C) $K_p = K_c = 0$
4.	(d) it has no effect	5.	(b) concentrated	6.	(d) zero
7.	(4) a, d				

Q1. Define chemical equilibrium?
Ans: Pg no 02

Q2: Define and explain following terms?
Ans: i) Microscopic events Pg no 2
ii) Dynamic equilibrium Pg no 2,29
iii) Le chatelier's principle Pg no 10
iv) Heterogenous equilibria Pg no 08
v) Homogenous equilibria. Pg no 08

Q3: Explain industrial application of Le chatelier's principle using Haber's process?
Ans Pg no 17

Q4. Propose microscopic events that account for the observed microscopic changes that take place during a shift in equilibrium.
Ans Macroscopic events are result of multiple microscopic events The microscopic events that explain the changes in equilibrium during chemical reaction are collisions and the formation of new bonds between particles and molecules. These collisions, changes the rates of forward and reverse reactions, which are affected by activation energy and external factors.

Qno5 Write kc and kp expression for following
Ans i) $SO_{2(g)} + 1/2\, O_{2(g)} \rightleftharpoons SO_{3(g)}$

$$kc = \frac{[Product]}{[reactant]} \qquad kp = \frac{P_{SO_3}}{P_{SO_2}\, P_{O_2}^{1/2}}$$

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

ii) $H_2O_{(g)} + Cl_2O \rightleftharpoons 2HOCl_{(g)}$

$$K_c = \frac{[HOCl]^2}{[H_2O][Cl_2O]} \qquad K_p = \frac{P_{HOCl}^2}{P_{H_2O} \times P_{Cl_2O}}$$

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

$$K_c = \frac{[O_2][O]}{[O_3]} \qquad K_p = \frac{P_{O_2} \times P_O}{P_{O_3}}$$

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

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

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

$$K_c = \frac{[H_2O]_g}{[H_2]} \qquad K_p = \frac{P_{H_2O}}{P_{H_2}}$$

ie, for kc and kp we don't write the reactant or product in liquid or solid state because they don't affect.

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

$$K_c = \frac{[NOCl]^2}{[NO]^2[Cl_2]} \qquad K_p = \frac{P_{NOCl}^2}{P_{NO}^2 \times P_{Cl_2}}$$

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

$$K_c = [CO_2] \qquad K_p = P_{CO_2}$$

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

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

Q no 6 At a particular temperature $K_p = 0.133$ atm. Which of the following conditions corresponds to equilibrium position.

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

a) $P_B = 0.175$ atm, $P_A = 0.102$ atm **c)** $P_B = 0.144$ atm, $P_A = 0.156$ atm
b) $P_B = 0.064$ atm, $P_A = 0.0308$ atm

$K_c = \frac{[B]^2}{[A]}$ $K_c = K_p$

a) $K_c = \frac{[0.175]^2}{[0.102]}$

$= 0.29$

b) $K_c = \frac{[0.064]^2}{[0.0308]}$

$= 0.29 \approx 0.3$

c) $K_c = \frac{[0.144]^2}{[0.156]}$

$= 0.133$

so answer is **b** and **c**

Q no 7 Write kc and kp.

solid copper II sulphate penta hydrate $\rightleftharpoons$ white solid copper + Water

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

$K_c = [H_2O]^5$ $K_p = P_{H_2O}^5$

Solid pentachloride phosphorus $\rightleftharpoons$ phosphours trichloride + chlorine

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

$K_c = [PCl_3][Cl_2]$ $K_p = P_{PCl_3} \times P_{Cl_2}$

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Q8 Predict the effect of reduced volume on following reactions

1 $PCl_{3(g)} + 3NH_{3(g)} \rightleftharpoons P(NH_2)_{3(g)} + 3HCl_{(g)}$

As moles of reactants = products = 4 So,
volume changes has no effect on this reaction.

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

When volume is reduced reaction proceeds in forward direction because of having lower number of moles.

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

Reduced volume brings the reaction in backward direction, because decrease in volume shifts equilibriume in the direction where molaar concentration is less.

Q9 Predict how the value of kc increases or decreases when temperature is increased for following reactions.

- $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\Delta H = +108kJ$

For endo thermic reaction increase in temperature brings reaction in the forward reaction.

$kc = \dfrac{[NO]^2 \leftarrow \text{increases}}{[N_2][O_2] \leftarrow \text{decreases}}$ so, value of kc increases.

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

For enothermic reaction increase in temperature proceeds reaction in reverse left direction

$kc = \dfrac{[SO_3]^2 \leftarrow \text{decreases}}{[SO_2]^2[O_2] \leftarrow \text{increases}}$ so, value of kc decreases.

- $N_2O_4(g) \rightleftharpoons 2N_2O_{2}$ $\Delta H = 58\,kJ$

For endothermic reaction proceed in forward direction when temperature increases.

$$K_c = \frac{[N_2O]^2}{[N_2O_4]} \begin{array}{l} \leftarrow \text{increases} \\ \leftarrow \text{decreases} \end{array}$$

so value of kc increases.

- $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = 256\,kJ$

For endothermic reaction proceeds in forward direction when temperature increases.

$$K_c = \frac{[CO][H_2]^3}{[CH_4][H_2O]} \begin{array}{l} \leftarrow \text{increase} \\ \quad \text{decrease} \end{array}$$

so value of kc increases.

Q10: What is the difference between an equilibrium with an kc value larger than one compared with an equilibrium that has a kc smaller than one?

$K_c > 1$ then the reaction proceeds in forward reaction

$K_c < 1$ then the reaction proceeds in reverse reaction.

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Q11: Describe the behaviour of following

1. Increasing pressure

$$C_3H_8(g) + 5O_2(g) \rightleftharpoons 3CO_2(g) + 4H_2O(g)$$

The reaction proceeds in reverse direction (towards low concentration)

2. Adding $I_2(g)$ to

$$2HI(g) \rightleftharpoons I_2(g) + H_2(g)$$

Proceeds in backward direction.

3. Removing heat

$$CO_2(g) \rightleftharpoons CO(g) + 1/2\,O_2(g) \quad \Delta H = 284\,kJ$$

temperature decrease for endothermic reaction causes reaction to proceed in backward direction.

Q12 $SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g) + \text{heat}$.
Predict 4 changes to decrease product yeild.
* if temperature is increased so reaction proceed towards left.
* if pressure is decreased reaction shift towards left.
* if volume is increased reaction shifts toward left.
* if SO_2Cl_2 is added or SO_2 and Cl_2 are removed.

Qno13 Predict change in volume to increase product yeild.

1. $Cl_2(g) + I_2(g) \rightleftharpoons 2ICl_2(g)$
There is no effect of volume.
Reason: Because molecule number is same for reactants & products.

2. $2NO_2(g) \rightleftharpoons N_2O_4(g)$
Volume should decreases to maximize product yeild.

Q14: $Cr_2O_7^{-2}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{-2}(aq) + 2H^+(aq)$

1. When sodium hydroxide is added:
Addition of NaOH causes H^+ to react so reaction proceeds in forward reaction.

2. hydrochloric acid added to solution:
Addition of HCl causes the yeild of product to decrease because HCl will produce H^+ ions in the solution so, the concentration of product increases causes equilibrium to shift in the opposite direction ie left.

Q15: The value of $k_c = 794$ at 298 k but 54 at 700k for following informatio. What would you deduce?

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The value of kc decreases when temperature increases - It means increase in termperature causes reaction to proceed in backward direction so, given reaction is exothermic reaction.

$$kc = \frac{[HI]^2}{[I_2][H_2]} \begin{array}{l} \leftarrow \text{decreases} \\ \leftarrow \text{increases.} \end{array}$$

- Product yeild:

Increase in temperature for this reaction decreases product yeild.

Q16 Propose a set of Conditions (V, P, T & concentration) for a reaction where enthalpy change is positive?

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)} \quad \Delta H = +58kJ$$

Effect of Concentration:

To increase product yeild N_2O_4 should be added or NO_2 should be removed from the reaction

Effect of Temperature:

To increase product yeild temperature should increased because it is an endothermic reaction, thus increase in temperature brings the reaction in forward direction.

Effect of Pressure:

Increase in pressure brings the reaction towards lower molar concentration ie reactant side so, for given reaction pressure should be reduced to enhance product yeild.

Effect of Volume:

If Volume is increased reaction proceed in forward direction towards higher concentration so maximum product would be get at increased volume.

Dynamic Equilibrium

At equilibrium stage the concentration of reactants and products becomes constant so reaction seems to stop however on microscopic level molecules are continuously reacting to give product and then molecules of products are continuously reacting to give reactants thus foward and reverse reactions are continuously happening.

The rate of forward reaction is equal to the rate of reverse reaction therefore it is a Dynamic equilibrium.

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