UNIT. NO 9 CHEMICAL EQUILIBRIUM

Complete Reaction:

Such a chemical reaction in which all the reactants have been converted into products is called a complete reaction.

Reversible Reaction:

Such a chemical reaction which proceeds in the forward direction as well as in the reverse direction under the same condition is called reversible reaction. In a reversible reaction the products can react together to re-form the original reactants. Reversible reactions never go to completion. The double arrow sign ($\rightleftharpoons$) is used to show a reversible reaction.

Examples:

$$2SO_2 + O_2 \underset{450\ C,\ 200atm}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3$$

$$N_2 + 3H_2 \underset{400\ C,\ 200atm}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

Chemical Equilibrium:

A state of a chemical reaction in which forward and reverse reactions take place at the same rate is called chemical equilibrium.

Chemical equilibrium is also called dynamic equilibrium. This is because reactions do not stop when they come to equilibrium state. The individual molecules keep on reacting continuously but there is no change in the actual amounts of reactants and products.

Example: 9.1

Write the forward and reverse reactions.

$$2NO + O_2 \rightleftharpoons 2NO_2$$

Forward Reaction:

The reaction from left to right is called forward reaction.

$$2NO + O_2 \longrightarrow 2NO_2$$

Reverse Reaction:

The reaction from right to left is called reverse reaction.

$$2NO \longrightarrow 2NO + O_2$$

Law of Mass Action

Question: **State law of mass action and derive relation for the equilibrium constant.**

Statement:

It states that the rate at which a substance reacts is directly proportional to its active mass and the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants.

Active mass:

Active mass represents the concentration of reactants and products in mol dm^{-3} for a dilute solution. Active mass is always expressed in terms of square brackets. [ ]

Explanation:

Consider a hypothetical reaction in which "a" moles of reactants "A" and "b" moles of reactant "B" react to give "c" moles of product "C" and "d" moles of product "D" at equilibrium.

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

According to law of mass action.

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

Rate of forward reaction $= (constant)\ [A]^a[B]^b$

Here constant = K_f

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

Now

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

Rate of reverse reaction $= (constant)[C]^c[D]^d$

Here constant = K_r

Rate of forward reaction = $K_r\ [C]^c[D]^d$

Here

K_f = constant for forward reaction and K_r = constant for reverse reaction

At equilibrium state

Rate of forward reaction = Rate of reverse reaction

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

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

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

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

Here

K_c is known as equilibrium constant and above expression is known as equilibrium constant expression.

Equilibrium Constant:

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

Equilibrium constant is defined as the ratio of the product of concentration of products to the product of concentration of reactants.

Conditions for Equilibrium:

Following conditions are required for equilibrium:

1. Concentration of reactants and products remains constant.
2. Temperature of the system remains constant.
3. Pressure or volume of the system remains constant.

Importance of Equilibrium Constant:

Equilibrium constant can be used to predict many important features of a chemical reaction.

1. It can be used to predict the direction of a chemical reaction.
2. It can be used to predict the extent of a chemical reaction.
3. It can be used to predict the effect of change in conditions of a chemical reaction.
4. It can be used to determine the equilibrium concentration of equilibrium mixture.

Page # 11 – Example # 9.2:

Coal can be converted to a gaseous fuel as methane. Coal reacts with hot steam to form CO and H_2. These gases can react further to give methane.

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

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

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

Q. Write equilibrium constant expression for this reaction.

Ans. $CO + 3H_2 \rightleftharpoons CH_4 + H_2O$

We know that equilibrium constant expression for this reaction is

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$K_c = \frac{[CH_4]^1[H_2O]^1}{[CO]\,[H_2]^3}$$

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Self Assessment Exercise 9.2:

1. **Following reaction can occur during lightning storms.**

$$3O_{2(g)d} \rightleftharpoons 2O_{3(g)}$$

Derive equilibrium constant expression for this reaction.

Ans. $3O_2 \rightleftharpoons 2O_3$

We know that equilibrium constant expression for this reaction is

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

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

2. **Write equilibrium constant expression.**

i. $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$

We know that equilibrium constant expression for this reaction is

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[H_2O]^2\,[Cl_2]^2}{[HCl]^4\,[O_2]^1}$$

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

We know that equilibrium constant expression for this reaction is

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[CH_3COOC_2H_5]^1\,[H_2O]}{[CH_3COOH]^1\,[C_2H_5OH]^1}$$

iii. $2HF \rightleftharpoons H_2 + F_2$

We know that equilibrium constant expression for this reaction is

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[H_2]^1\,[F_2]^1}{[HF]^2}$$

iv. $2NO_2 \rightleftharpoons N_2O_4$

We know that equilibrium constant expression for this reaction is

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[N_2]\,[O_4]}{[NO_2]^2}$$

Units of Equilibrium Constant:

Equilibrium constant may or may not have a unit. To find unit of equilibrium constant we used two steps.

Step:1

Write equilibrium constant expression.

Step:2

Write units of concentration of reactants and products.

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Example 9.3: Determine units of equilibrium constant.

Determine the units of equilibrium constants for the following reaction.

1. $H_2 + I_2 \rightleftharpoons 2HI$

Solution:

We know

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[HI]}{[H_2][I_2]}$$

Write units of concentration

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}][moldm^{-3}]}$$

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}]^2}$$

= No units

2. $N_2O_4 \rightleftharpoons 2NO_2$

Solution:

We know

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

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

Write units of concentration

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}]}$$

$$Kc = moldm^{-3}$$

3. $2NO_2 + O_2 \rightleftharpoons 2NO_2$

Solution:

We know

$$Equilibrium\ constant = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

Write units of concentration

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}]^2[moldm^{-3}]}$$

$$Kc = [moldm^{-3}]^{-1}$$

$$Kc = [mol^{-1}dm^{3}]$$

$$Kc = mol^{-1}dm^{-3}$$

Self Assessment Exercise 9.3:

Determine the units of equilibrium.

1. $N_2 + O_2 \rightleftharpoons 2NO$

We know

$$Kc = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[NO]^2}{[N_2][O_2]^{-1}}$$

Write units of concentration

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}][moldm^{-3}]}$$

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}]^2}$$

= No units

2. $H_2 + CO_4 \rightleftharpoons H_2O + CO$

We know

$$Kc = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[H_{2O}]^1[CO]^1}{[H_2][CO_2]^1}$$

Write units of concentration

$$Kc = \frac{[moldm^{-3}]^1[moldm^{-3}]^1}{}$$

$[moldm^{-3}]^1[moldm^{-3}]^1$

$$Kc = \frac{[moldm^{-3}]^2}{[moldm^{-3}]^2}$$

= **No units**

3. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

We know

$$K_c = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$K_c = \frac{[PCl_3]^1[Cl_2]^1}{[PCL_5]^1}$$

Write units of concentration

$$K_c = \frac{[moldm^{-3}]^1[moldm^{-3}]^1}{[moldm^{-3}]^1}$$

$$K_c = \frac{[moldm^{-3}]^2}{[moldm^{-3}]^1}$$

$$K_c = moldm^{-3}$$

4. $CO + 2H_2 \rightleftharpoons CH_3OH$

We know

$$Kc = \frac{Product\ of\ concentration\ of\ products}{Product\ of\ concentration\ of\ reactants}$$

$$Kc = \frac{[CH_3OH]^2}{[CO]^1[H_2]^2}$$

Write units of concentration

$$Kc = \frac{[moldm^{-3}]^1}{[moldm^{-3}]^1\ [moldm^{-3}]^2}$$

$$Kc = [moldm^{-3}]^{-2}$$

$$Kc = mol^{-2}dm^6$$

Hyber's Process:

Ammonia is produced on the large scale by a special process known as hyber's process. In this process nitrogen react with hydrogen at 450°C, 200atm pressure and in the presence of catalyst and as a result ammonia is produced.

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

This is a reversible process and produced only 33% ammonia at equilibrium. The high pressure is used to favour the formation of ammonia, but after cooling the equilibrium mixture gives 98% ammonia.

Contact Process:

Sulphuric acid is produced on the large scale by a special process known as contact process. In this process first of all sulphur react with oxygen and produced sulphuric dioxide.

$$S + O_2 \longrightarrow SO_2$$

In second step sulphuric dioxide is purified and again react with oxygen at 450°C and 200atm pressure in the presence of Pt or V_2O_5 as catalyst.

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

This reaction is reversible and by using principle of chemical equilibrium maximum amount of SO_2 is converted into SO_3. In last step SO_3 react with water and produce 100% pure sulphuric acid.

Q. Define catalyst?

Ans. A catalyst is a substance which increases the rate of a chemical reaction. Catalysts reduce the time taken to reach equilibrium state, but they have no effect on the position of equilibrium.

Q. What is the proper way of adding acid and water?

Ans. The addition of water to the concentrated sulphuric acid produces a vigorous reaction. As a result of this reaction the acid droplets spread in all direction. Therefore avoid adding water to the acid and always add acid to water when diluting it.

Q. What type of reaction takes place in fizzy drinks?

Ans. When fizzy drinks are made, CO_2 is dissolved in the liquid drink under pressure and scaled. When you remove lid of the bottle, bubbles of CO_2 suddenly appear. When you put the lid back on the bottle, the bubbles stop. This is due to the following equilibrium.

$$CO_2 \rightleftharpoons CO_2$$

The forward reaction happens during manufacturing and the reverse reaction happens and opening.

<u>Review Questions</u>:

Q2. Give short answer.

i) Differentiate b/w forward and reverse reactions.

Forward Reaction	Reverse Reaction
The reaction written from left to right is called forward reaction.	The reaction written from right to left is called reverse reaction.
In this case reactants react together to give products.	In this case products react together to give reactants.