CHEMISTRY

Class

10

Published by

Leading Books Publisher

Khyber Pakhtunkhwa Textbook Board Peshawar

Developed according to National Curriculum 2006 and approved by DCTE Abbottabad.
Vide No. 5248-51/SS-II, dated: 17-9-2012

Authors: Mushtaq-ur-Rehman, Prof. Aslam Khan, Prof. Nazeer Ahmad, Mr. Musharaf Khan

Review Supervision:

Syed Bashir Hussain Shah Director DCTE, Abbottabad.

Reviewers:

Mr. Muhammad Sajjad Khan Associate Prof: of Chemistry GPGC No.1 Abbottabad.
Mr.Ibn-e-Yamin, SET GHS Dhamtour Abbottabad.
Mr. Faisal Khan, SS GHSS Bandi Dhundan Abbottabad.
Mr. Muhammad Amin, Ex-SS, Textbook Board, Peshawar.
Mr. Abrar Ahmad, SS, DCTE Khyber Pakhtunkhwa Abbottabad.

Editor: **Salmana Zaman Khan SS (Science)**
Khyber Pakhtunkhwa Textbook Board Peshawar.

Printing Supervision:

Masood Ahmad, Chairman,
Saeedur Rehman, Member E & P,
Khyber Pakhtunkhwa Textbook Board Peshawar.

Academic Year 2018-19
Website: www.kptbb.gov.pk
Email : membertbb@yahoo.com
Phone: 091-9217159-60

CONTENTS

Chapter

9

Chemical Equilibrium

In this chapter you will be able to:

- Define chemical equilibrium in terms of a reversible reaction.
- Write both the forward and the reverse reactions and describe the macroscopic characteristics of each.
- Define Law of mass action.
- Derive an expression for the equilibrium constant and its units.
- State the necessary conditions for equilibrium and the ways that equilibrium can be recognized.
- Write the equilibrium constant expression of a reaction.

9 Introduction

Consider a closed container partially filled with a liquid at a given temperature. Molecules escape from the liquid into the vapour phase and are collected in the free space above the liquid. Some of the vapour molecules start to condense back into the liquid state. Initially the rate of condensation is slower than that of evaporation. But as more and more vapours are formed the rate of condensation increases and utlimately becomes equal to the rate of evaporation. At this stage both evaporation and condensation continue to take place without any net change. This system is said to be in a state of dynamic equilibrium.

$$\underset{\text{(Water)}}{\text{liquid}} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \underset{\text{(vapours)}}{\text{gas}}$$

9.1 Reversible Reactions and Dynamic Equilibrium

Consider the following reaction,

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

This reaction proceeds in the forward direction but as soon as some amount of ammonia is formed the ammonia molecules dissociate into nitrogen and hydrogen and the reaction is reversed.

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

Such reactions which proceed in the forward as well as in the reverse direction are called *reversible reactions*. Most of the reactions are reversible. A reversible reaction can be represented by two arrows ($\rightleftharpoons$) between the reactants and products. For example, the above reaction can be written as follows.

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

Other examples are given below.

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

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

Let us consider a general reaction in which A reacts with B in the gaseous state in a closed vessel forming products C & D.

$$A_{(g)} + B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

The initial concentration of A and B is taken the same, while that of the products C and D is zero. As the forward reaction proceeds, the concentrations of the reactants (A,B) decrease and the concentration of the products (C,D) increase continuously. Therefore, the rate of forward reaction decreases and that of backward reaction increases. Ultimately, a stage reaches when the rate of forward reaction becomes equal to the rate of backward reaction. At this stage the concentrations of the reactants and products become constant. Reaction at this stage is said to be at the state of equilibrium.

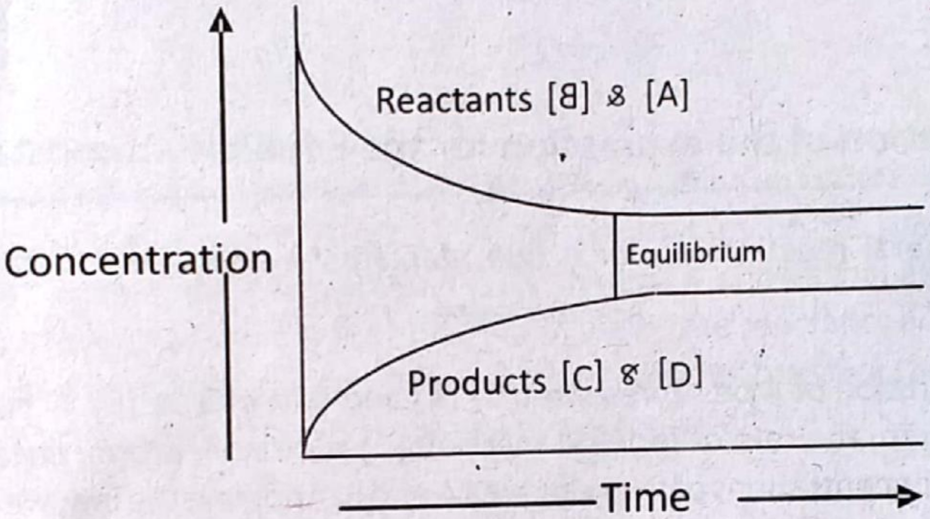

Fig. 9.1 Reversible Reaction and equilibrium state

At the equilibrium state, it seems that the reaction has stopped since no more product is formed. Actually the reaction continues and the amount of the products formed is transformed back into the reactants. Such an equilibrium in the reversible reactions is called the dynamic equilibrium.

Society, Technology and Science

Nitrogen and oxygen are important components of the atmosphere. These are used successfully in the industrial preparation of nitric acid (Birkland-Eyde process), which is a very important chemical.

In this process air is passed through electric arc to obtain nitric oxide.

$$N_2 + O_2 \rightleftharpoons 2NO$$

The nitric oxide is further oxidized to NO_2 in the presence of oxygen.

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

The NO_2 gas is dissolved in water in the absorption tower and nitric acid is formed

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

9.2 Law of mass action

This law was suggested by two chemists, Guldberg and Waage in 1864. It gives a relation between the concentrations of reactants and products at equilibrium in a chemical reaction. This law states that "the rate or speed of a chemical reaction is proportional to the product of the active masses of the reacting substances". By the term active mass we mean the molar concentration, or number of moles per dm^3 in a dilute solution.

9.2.1 Derivation of the expression for the Equilibrium constant

Consider a general reaction in which two reactants A and B react to form the products C and D.

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

Let the concentration of A be represented by [A] and that of B by [B]. According to law of mass action, the rate of forward reaction (r_1) is directly proportional to the product of the concentrations of the reactants A and B. Applying the law, we get.

$$\text{Rate of forward reaction} = r_1 \propto [A][B]$$

Replacing the sign of proportionality by equality sign we introduce a proportionality constant, k_1 and the above equation becomes,

$$r_1 = k_1[A][B]$$

Here k_1 is the rate constant for the forward reaction.

The reaction under study is a reversible reaction. As the products C and D are formed they react back and are converted into the reactants, A and B. For the reverse reaction.

$$\text{Rate of reverse reaction} = r_2 \propto [C][D]$$

$$r_2 = k_2[C][D]$$

Where, k_2 is the rate constant for the reverse reaction.

At equilibrium,
the rate of forward reaction = the rate of reverse reaction

$$r_1 = r_2$$

Therefore,

$$k_1 [A] [B] = k_2 [C] [D]$$

$$\frac{k_1}{k_2} = \frac{[C] [D]}{[A] [B]}$$

Therefore $K_c = \frac{[C] [D]}{[A] [B]}$ $K_c' = \frac{k_1}{k_2}$

Where, K_c is called the equilibrium constant. The equilibrium constant, K_c may be defined as the ratio of the product of the active masses of the products to the product of active masses of reactants. A large value of K_c shows that at equilibrium, the product concentrations are greater than those of the reactants and vice versa. The equilibrium constant of a reaction is independent of pressure, concentration and catalyst and its value is constant for a particular reaction.

Example 9.1

We have the values of Kc as:
i) 10^2 ii) 10^{30} iii) 10^{-30} and iv) 1
Which value of Kc for the following reaction, predicts that the reaction goes to completion in the forward direction:

Solution: $CaCO_3 \rightleftharpoons CaO + CO_2$

$$K_c = \frac{[CaO] [CO_2]}{[CaCO_3]}$$

Since the reaction goes to completion in the forward direction, the concentration of the products is much more as compared to the reactants and the value of K_c would be very large. Hence, the answer is ii) 10^{30}.

Activity

Write equilibrium constant expression for the following reversible reactions.

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

$$PC\ell_{3(g)} + C\ell_{2(g)} \rightleftharpoons PC\ell_{5(g)}$$

9.3 Equilibrium constant and its Units

Equilibrium constant is a ratio of the product of the concentrations of the products to the product of the concentrations of the reactants. Hence the unit of K_c depends on the equilibrium constant expression for the given reaction. For example if number of moles of reactants and products are equal, the equilibrium constant has no units as concentration units cancel out.

Example 9.2 What is the unit of K_c if one mole of each reactant and product is present in the equilibrium mixture of the following reaction?

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

Solution Writing equilibrium constant expression, we get no units for K_c for the above reaction.

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{[1\ \text{mole dm}^{-3}] \times [1\ \text{mole dm}^{-3}]}{[1\ \text{mole dm}^{-3}]^2}$$

9.4 Equilibrium calculations

The value of equilibrium constant can be calculated if we know the concentrations of the reactants and products in the equilibrium mixture.

Example 9.3

In the equilibrium mixture, the concentration of hydrogen and iodine is 0.04 moles per dm^3 each while that of hydrogen iodide is0.08 mole per dm^3. Find K_c of the following reaction.

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

Solution

Writing the equilibrium constant expression for the above reaction.

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

$$K_c = \frac{[0.08]^2}{[0.04][0.04]} = 4$$

9.5 Importance (applications) of equilibrium constant

The value of equilibrium constant is specific and remains constant at a particular temperature. The value of K_c helps us to predict:

(i) Direction of reaction

We know that, $K_c = \frac{[products]}{[reactants]}$ for any reaction

The direction of a chemical reaction at any particular time can be predicted by means of [products]/[reactants] ratio. The value of [products]/[reactants] ratio leads to one of the following three possibilities.

(a) The ratio is less than K_c. This implies that more of the product is required to attain the equilibrium, therefore, the reaction will proceed in the forward direction.

(b) The ratio is greater than K_c. It means that the reverse reaction will occur to attain the equilibrium.

(c) When the ratio is equal to K_c, then the reaction is at equilibrium.

(ii) Extent of Reaction

(a) If the equilibrium constant is very large, this indicates that the reaction is almost complete.

(b) If the value of Kc is very small, it reflects that the reaction does not proceed appreciably in the forward direction.

(c) If the value of Kc is moderate this shows a very little forward reaction.

(iii) The effect of external conditions on the position of equilibrium

When a system reaches equilibrium it will remain in same state indefinitely if the conditions do not change. However, the equilibrium state of a system is disturbed if external conditions are changed, e.g, change of pressure, temperature and concentrations of reactants and products alter the position of the equilibrium. Whenever, the equilibrium is disturbed by changes in the external conditions, the system always tends to restore equilibrium.

9.6 *Conditions for equilibrium*

The following are the conditions of chemical equilibrium.

(I) When a chemical equilibrium is established in closed vessel at constant temperature concentration of various species in the reaction become constant. The concentrations are called equilibrium concentration.

(ii) Equilibrium cannot be attained in open vessel. In an open vessel the gaseous reactants and products may escape into atmosphere leaving behind no possibility of attaining equilibrium.

(iii) A catalyst cannot change the equilibrium point, it only speeds up the rate of both the forward and the reverse reaction.

The experimental methods used for the determination of the equilibrium constant, depend on the nature of reactants and temperature. Two types of procedures have been used.

In the first of these the reacting substances are sealed into glass bulbs and allowed to attain equilibrium and contents are analyzed. The second procedure is the "flow method", in which the gases are passed through a tube and equilibrium mixture is analyzed. When concentration of equilibrium mixture becomes constant, the equilibrium is established. This is the principal criterion of chemical equilibrium.

KEY POINTS

- The reaction that does not go to completion and the products formed react to form the reactants back is called a reversible reaction.
- A state of dynamic equilibrium is established when the rate of forward reaction becomes equal to the rate of reverse reaction.
- The reversible reaction when reaches the equilibruim stage, no more changes in concentrations of reactants and products take place.
- The rate at which a substance reacts, is directly proportional to its active mass and the rate of reaction is directly proportional to the product of active masses of the reacting substances. Active mass or activity "a" is directly proportional to the molar concentration "c".
- *Equilibrium Constant of the reaction,* K_c is defined as the ratio of the product of the molar concentration of the products to that of the reactants. A very large value of equilibrium constant, K_c indicates that the reaction is almost complete. If the value of K_c is very small, then the reaction proceeds a little in the forward direction.
- The equilibrium constant can be used to predict the direction in which a chemical system would proceed to acquire the equilibrium state.

EXERCISE

1. *Choose the correct answers from the given options*

i. Consider the system :

Water(l) $\rightleftharpoons$ Water(g)

At dynamic equilibrium:

A) reversible reaction stops
B) amount of liquid water and water vapour is the same
C) amount of liquid water and water vapour is constant
D) Amount of liquid is minimum

ii. A reversible reaction proceeds in the:

A) reverse direction
B) forward direction
C) forward and reverse direction
D) more backward less forward

iii. The equilibrium constant (K_c) is:

A) The sum of the two rate constants
B) The difference of the two rate constants
C) The ratio of the two rate constants
D) The product of the two rate constants

iv. For the reaction A + B $\rightleftharpoons$ C + D

K_c is equal to:

A) $\frac{[A]+[B]}{[C]+[D]}$ B) $\frac{[A]+[D]}{[B]+[C]}$

C) $\frac{[A][B]}{[C][D]}$ D) $\frac{[C][D]}{[A][B]}$

v. For a reaction $N_{2(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{(g)}$

if $K_C = 10^{-30}$ at 25°C. One can predict:

A) More NO is formed
B) The forward reaction goes to completion

C) The backward reaction goes to completion
D) More reactants are consumed

vi. The unit of Kc for the following system is:

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$,

A) mol^2/L^2 B) L/mol
C) mol/L^2 D) mol/dm^3

vii. Molecules of chlorine do not decompose into atomic chlorine i.e:

$Cl_2 \rightleftharpoons 2\dot{Cl}$

This is because K_c of this reaction is:

A) Very large B) Very small
C) Zero D) 1

viii. How much reaction is complete when $K_c = 1$:

A) 10% B) 25%
C) 50% D) 100%

2. Write Short answers to the following questions

i. Give an expression for K_c for the following reversible reactions.

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

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

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

ii. Define law of mass action
iii. Write down the units of K_c.
iv. What are reversible and irreversible reactions?
v. What is dynamic equilibrium?

3. Write long answers to the following questions?

I. What is the importance of equilibrium constant?
ii. Write down the conditions necessary for equilibrium.
iii. What is equilibrium constant? Explain its units.