
CHAPTER

9

Chemical Equilibrium

*Animation 9.1 : synthesis
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Students Learning Outcomes

Students will be able to:

- Define chemical equilibrium in terms of a reversible reaction. (Understanding);
- Write both the forward and the reverse reaction and describe the macroscopic characteristics of each. (Applying);
- Define Law of Mass Action. (Understanding);
- Derive an expression for the equilibrium constant and its units. (Applying);
- State the necessary condition for the equilibrium and the ways that equilibrium can be recognized. (Understanding) and
- Write the equilibrium constant expression of a reaction.

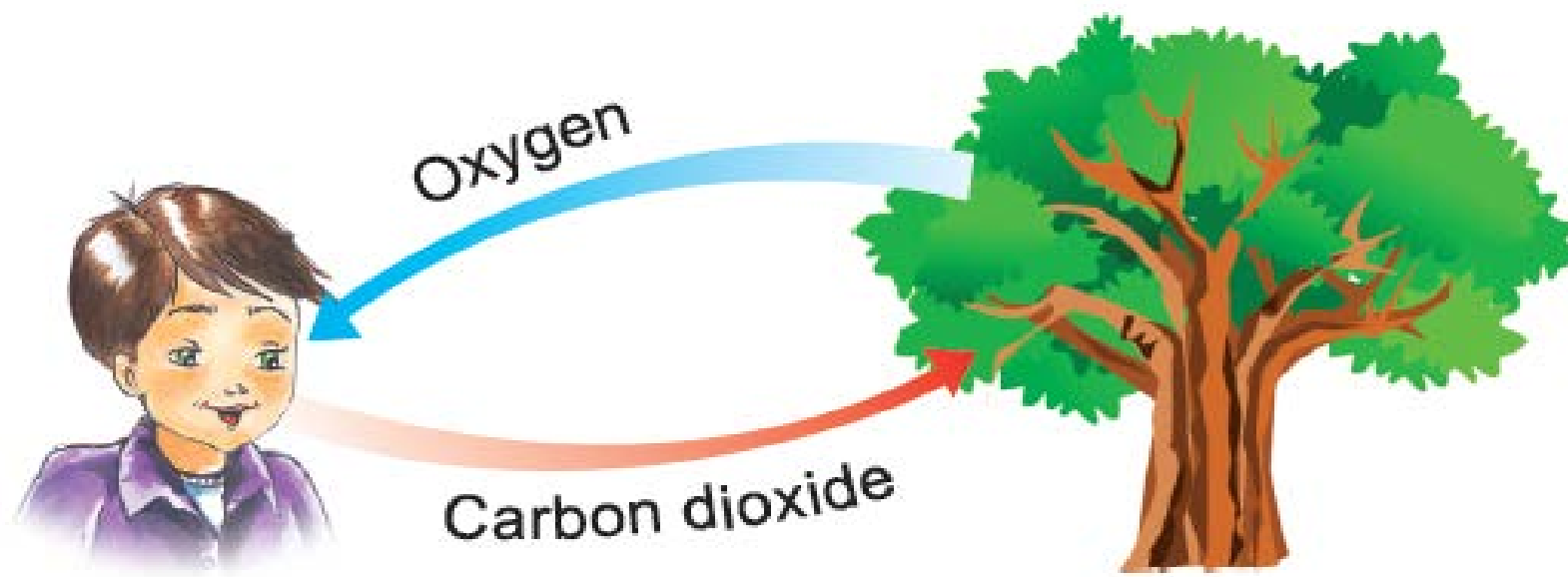
Introduction

Generally, we presume that most chemical and physical changes proceed to completion. A complete reaction is one in which all reactants have been converted into products. However, most chemical reactions do not go to completion because products react themselves to form the reactants. As a result, after sometime no further change takes place. Quantities of reactants and products remain unchanged and it seems that the reaction has stopped. In fact, these reactions do not stop; rather they take place on both directions at equal rate and attain the equilibrium state. Such reactions are called reversible reactions. Many examples of physical and chemical equilibrium are found in nature.

We owe our existence to equilibrium phenomenon taking place in atmosphere. We inhale oxygen and exhale carbon dioxide, while plants consume carbon dioxide and release oxygen. This natural process is responsible for the existence of life on the Earth.

Many environmental systems depend for their existence on delicate equilibrium phenomenon. For example, concentration of gases in lake water is governed by the principles of equilibrium.

The lives of aquatic plants and animals are indirectly related to concentration of dissolved oxygen in water.



9.1 REVERSIBLE REACTION AND DYNAMIC EQUILIBRIUM

In a chemical reaction, the substances that combine are called reactants and the new substances formed are called products. For example, when H_2 and O_2 (reactants) combine they form H_2O (product).

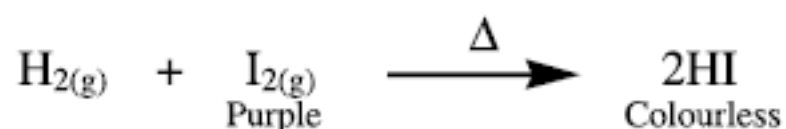


Most of the reactions, in which the products do not recombine to form reactants, are called **irreversible reactions**. They are supposed to complete and are represented by putting a single arrow (\longrightarrow) between the reactants and products.

On the other hand, reactions in which the products can recombine to form reactants are called **reversible reactions**. These reactions never go to completion. They are represented by a double arrow (\rightleftharpoons) between reactants and products. These reactions proceed in both ways, i.e., they consist of two reactions; forward and reverse. So, a reversible reaction is one which can be made to proceed in either direction depending upon the conditions.

Let us discuss a reaction between hydrogen and iodine. Because one of the reactants, iodine is purple, while the product hydrogen iodide is colourless, proceedings of the reaction are easily observable. On heating, hydrogen and iodine.

vapours in a closed flask, hydrogen iodide is formed. As a result, purple colour of iodine fades as it reacts to form colourless hydrogen iodide, as shown in figure 9.1.



This reaction is called as forward reaction.

On the other hand, when only hydrogen iodide is heated in a closed flask, purple colour appears because of formation of iodine vapours. Such as



In this case, hydrogen iodide acts as reactant and produces hydrogen and iodine vapours. This reaction is reverse of the above. Therefore, it is called as **reverse reaction**.

When both of these reactions are written together as a reversible reaction, they are represented as:

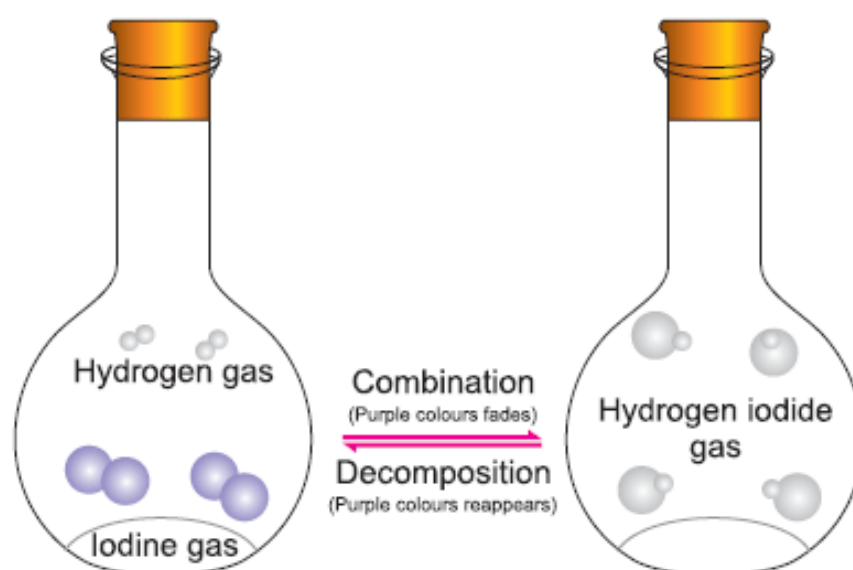
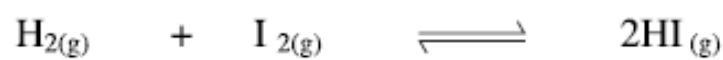
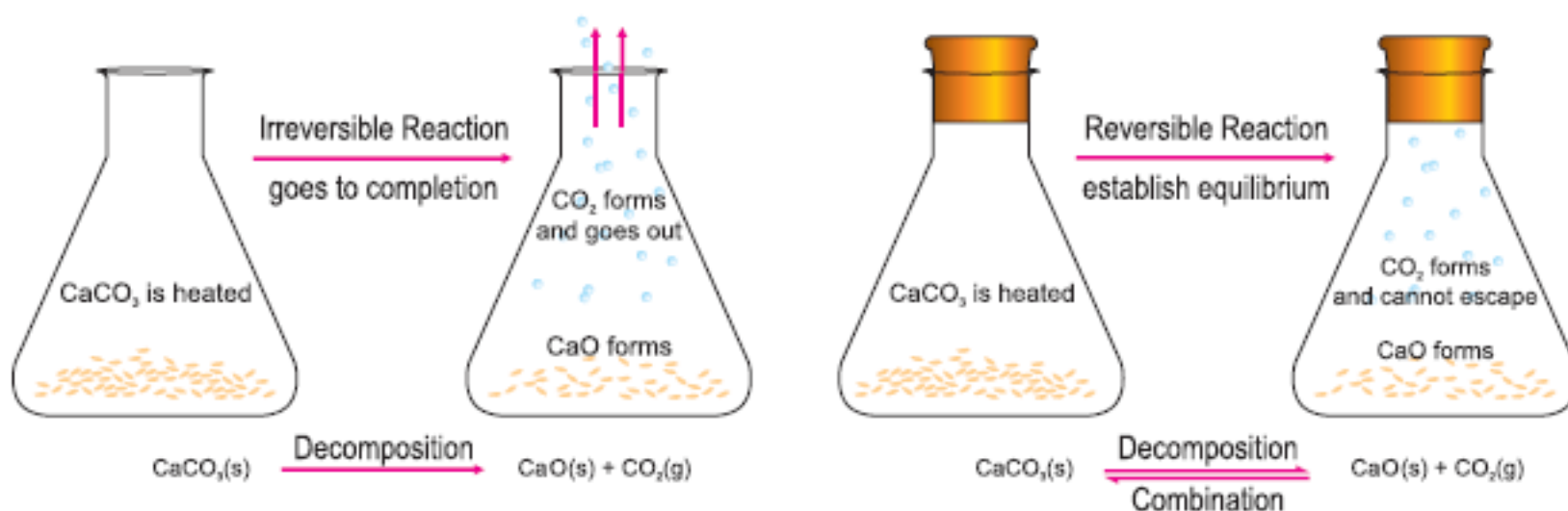
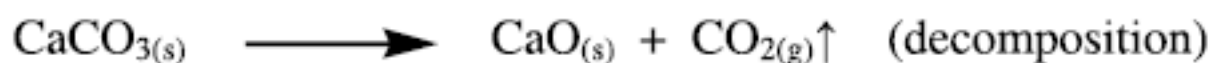


Fig. 9.1 Showing establishment of reversible reaction.

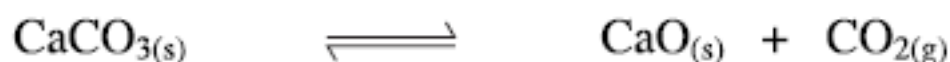
Let us have another example, when calcium oxide and carbon dioxide react, they produce calcium carbonate:



On the other hand, when CaCO_3 is heated in an open flask, it decomposes to form calcium oxide and carbon dioxide. CO_2 escapes out and reaction goes to completion:



In these two reactions, decomposition is reverse to combination or vice versa. When calcium carbonate is heated in a closed flask, so that CO_2 can't escape out as shown in figure 9.2. Initially only decomposition take place on (forward reaction), but after a while CO_2 starts combining with CaO to form CaCO_3 (reverse reaction). In the beginning, forward reaction is fast and reverse reaction is slow. But eventually, the reverse reaction speeds up and both reactions go on at the same rate. At this stage, decomposition and combination take place at the same rate but in opposite directions, as a result amounts of CaCO_3 , CaO and CO_2 do not change. It is written as



When we think of the term equilibrium, the first word that usually comes to mind is “balance”. However, the balance may be achieved in a variety of ways.

*Thus, when the rate of the forward reaction is the same as the rate of reverse reaction, the composition of the reaction mixture remains constant, it is called a **chemical equilibrium state**.*

At equilibrium state there are two possibilities.

1. When reaction ceases to proceed, it is called static equilibrium. This happens mostly in physical phenomenon. For example, a building remains standing rather than falling down because all the forces acting on it are balanced. This is an example of static equilibrium.
2. When reaction does not stop, only the rates of forward and reverse reactions become equal to each other but take place in opposite directions. This is called dynamic equilibrium state. Dynamic means reaction is still continuing. At dynamic equilibrium state:

Rate of forward reaction = Rate of reverse reaction

In a reversible reaction, dynamic equilibrium is established before the completion of reaction. It is represented graphically in figure 9.3. At initial stage, the rate of forward reaction is very fast and reverse reaction is taking place at a negligible rate. But gradually forward reaction slows down and reverse reaction speeds up. Eventually, both reactions attain the same rate, it is called a **dynamic equilibrium state**.

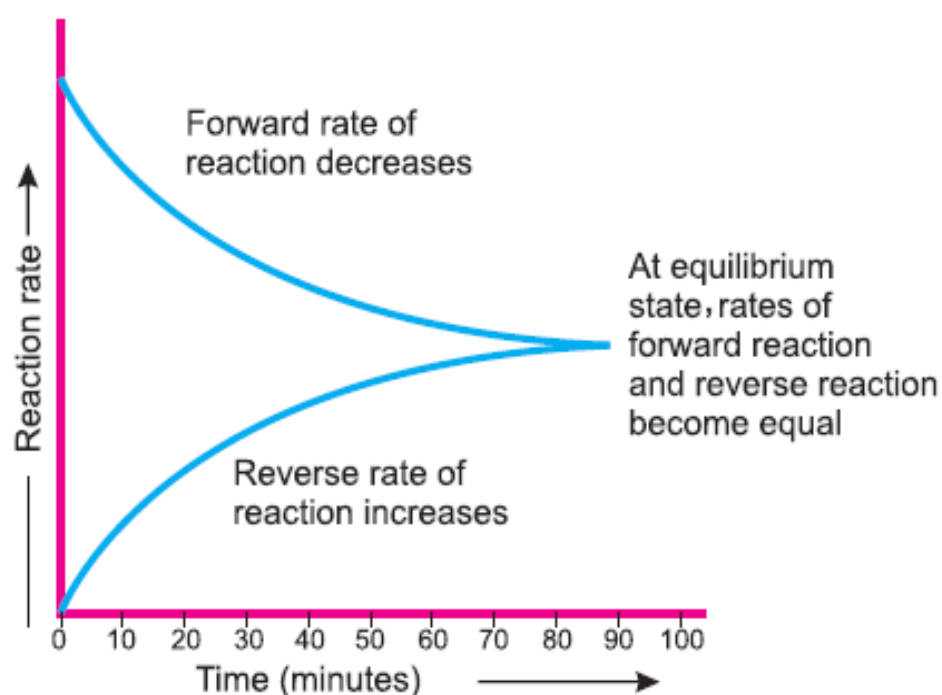


Fig. 9.3 Graph showing the rate of forward and reverse reactions and establishment of equilibrium state

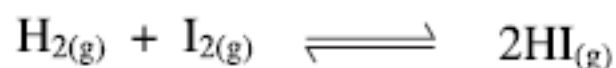
For example, in case of reaction between hydrogen and iodine vapours, some of the molecules react with each other to give hydrogen iodide.



At the same time, some of the hydrogen iodide molecules decompose back to hydrogen and iodine.



In the beginning, as the concentration of the reactants is higher than that of the products, the rate of the forward reaction is faster than the reverse reaction. As the reaction proceeds, the concentration of reactants will gradually decrease while that of product will increase, consequently the rate of the forward reaction will go on decreasing and the reverse reaction will go on increasing and ultimately the two rates will become equal to each other. Thus, the equilibrium will set up and concentration of various species ($\text{H}_2, \text{I}_2, \text{HI}$) becomes constant. It is represented as



Macroscopic characteristics of forward and reverse

Forward Reaction	Reverse Reaction
<ol style="list-style-type: none"> 1. It is a reaction in which reactants react to form products. 2. It takes place from left to right. 3. At initial stage, the rate of forward reaction is very fast. 4. It slows down gradually 	<ol style="list-style-type: none"> 1. It is a reaction in which products react to produce reactants. 2. It takes place from right to left. 3. In the beginning, the rate of reverse reaction is negligible. 4. It speeds up gradually.

Macroscopic characteristics of dynamic equilibrium

A few important characteristic features of dynamic equilibrium are given below:

1. An equilibrium is achievable only in a closed system (in which substances can neither leave nor enter).
2. At equilibrium state, a reaction does not stop. Forward and reverse reactions keep on taking place at the same rate but in opposite direction.
3. At equilibrium state, the amount (concentration) of reactants and products do not change. Even physical properties like colour, density, etc. remain the same.

- An equilibrium state is attainable from either way, i.e. starting from reactants or from products.
- An equilibrium state can be disturbed and again achieved under the given conditions of concentration, pressure and temperature.

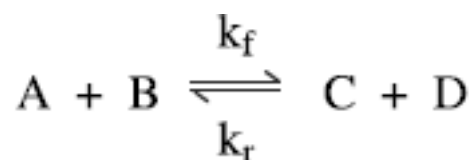


- Why reversible reactions never complete?
- What is a static equilibrium, explain with an example.
- Why the amounts of reactants and products do not change in a reversible reaction.

9.2 LAW OF MASS ACTION

Guldberg and Waage in 1869 put forward this law. According to this law “The rate at which a substance reacts is directly proportional to its active mass and the rate of a reaction is directly proportional to the product of the active masses of the reacting substances”. Generally, an active mass is considered as the molar concentration having units of mol dm^{-3} , expressed as square brackets [].

For example, consider a reversible reaction of the type



Suppose [A], [B], [C] and [D] are the molar concentrations (mol dm^{-3}) of A, B, C and D respectively.

According to the Law of Mass Action:

$$\begin{aligned} \text{The rate of the forward reaction} &\propto [A][B] \\ &= k_f [A][B] \end{aligned}$$

Similarly,

$$\begin{aligned} \text{The rate of the reverse reaction} &\propto [C][D] \\ &= k_r [C][D] \end{aligned}$$

where k_f and k_r are the proportionality constant called specific rate constants of the forward and the reverse reactions, respectively.

At equilibrium state:

The rate of forward reaction = The rate of reverse reaction

$$k_f [A][B] = k_r [C][D]$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$\text{Where } K_c = \frac{k_f}{k_r}$$

K_c is called equilibrium constant. It is represented as:

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

Law of Mass Action describes the relationship between active masses of the reactants and the rate of a reaction.

Derivation of the Expression for Equilibrium Constant for General Reaction

Let us apply the law of Mass Action for a general reaction.



This reaction consists of two reactions; forward and reverse reactions. According to this law, **the rate of a chemical reaction is directly proportional to the product of the molar concentrations of its reactants raised to power equal to their number of moles in the balanced chemical equation of the reaction.**

Let us first discuss the forward reaction. A and B are the reactants whereas 'a' and 'b' are their number of moles.

The rate of forward reaction according to law of Mass Action is:

$$R_f \propto [A]^a[B]^b$$

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

where k_f is the rate constant for the forward reaction. Similarly, the rate of the reverse reaction R_r is directly proportional to the product of $[C]^c [D]^d$, where 'c' and 'd' are the number of moles as given in the; of $[C]^c [D]^d$, where 'c' balanced chemical equation. Thus,

$$R_r \propto [C]^c [D]^d$$

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

where k_r is the rate constant for the reverse reaction. We know that at equilibrium state the rates of both the reactions are equal.

The rate of forward the reaction = The rate of the reverse reaction

Such as:

$$R_f = R_r$$

and putting the values of R_f and R_r

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

By taking the constants on one side and the variables on other side of the equation, the above equation becomes:

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

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

where, $\left| K_c = \frac{k_f}{k_r} \right|$ is called equilibrium constant.

This expression is for chemical equilibrium constant. All the reversible reactions can be expressed in this form. Such as:

1. When nitrogen reacts with oxygen to form nitrogen monoxide, the reversible reaction is as follows



The rate of forward reaction

$$R_f = K_f [\text{N}_2] [\text{O}_2]$$

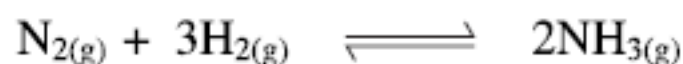
The rate of reverse reaction

$$R_r = K_r [\text{NO}]^2$$

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$

2. For the reaction of nitrogen with hydrogen to form ammonia, the balanced chemical equation is



For the reaction

The rate of forward reaction $R_f = K_f [N_2] [H_2]^3$

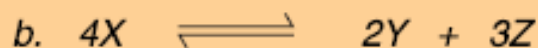
The rate of reverse reaction $R_r = K_r [NH_3]^2$

The expression for the equilibrium constant for this reaction is:

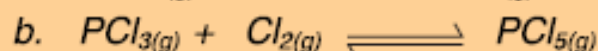
$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$



1. Define the Law of Mass Action.
2. How is the active mass represented?
3. What do you mean by equilibrium constant?
4. Point out the coefficients of each in the following hypothetical reactions:



5. Write the equilibrium constant expressions for the following reactions:



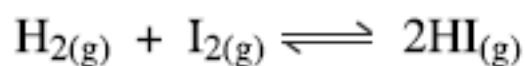
9.3 EQUILIBRIUM CONSTANT AND ITS UNITS

Equilibrium constant is a ratio of the product of concentration of products raised to the power of coefficient to the product of concentration of reactants raised to the power of coefficient as expressed in the balanced chemical equation.

$$K_c = \frac{\text{Product of concentration of products raised to the power of coefficients}}{\text{Product of concentration of reactants raised to the power of coefficients}}$$

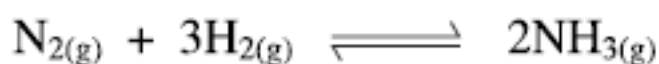
It is conventional to write the products as numerator and reactants as denominator. By knowing, the balanced chemical equation for a reversible reaction we can write the equilibrium expression. Thus, we can calculate the numerical value of by putting actual equilibrium concentrations of the reactants and products into equilibrium expression. The value of K_c depends only on temperature, it does not depend on the initial concentrations of the reactants and the products. A few problems have been solved to make the concept clear.

K_c has no units in reactions with equal number of moles on both sides of the equation. This is because concentration units cancel out in the expression for K_c , e.g., for the reaction:



$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \quad \text{Units} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})} = \text{no units}$$

For reactions in which the number of moles of reactants and product are not equal in the balanced chemical equation, K of course, have units, e.g., for the reaction



$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(\text{mol dm}^{-3})^2}{(\text{mol dm}^{-3})(\text{mol dm}^{-3})^3} = \frac{1}{(\text{mol dm}^{-3})^2} = \text{mol}^{-2} \text{dm}^6$$

Problem 9.1

When hydrogen reacts with iodine at 25 °C to form hydrogen iodide by a reversible reaction as follows:



The equilibrium concentrations are:

$$[\text{H}_2] = 0.05 \text{ mol dm}^{-3}; \quad [\text{I}_2] = 0.06 \text{ mol dm}^{-3}; \quad \text{and} \quad [\text{HI}] = 0.49 \text{ mol dm}^{-3}.$$

Calculate the equilibrium constant for this reaction.

Solution

Given equilibrium concentrations are;

$$[\text{H}_2] = 0.05 \text{ mol dm}^{-3}; \quad [\text{I}_2] = 0.06 \text{ mol dm}^{-3}; \quad \text{and} \\ [\text{HI}] = 0.49 \text{ mol dm}^{-3}.$$

Write the equilibrium constant expression as

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

Now, put the values of equilibrium concentrations in equilibrium expression:

$$K_c = \frac{[0.49]^2}{[0.05][0.06]} = \frac{0.2401}{0.0030} = 80$$

Problem 9.2

For the formation of ammonia by Haber's process, hydrogen and nitrogen react reversibly at 500 °C as follows



The equilibrium concentrations of these gases are: nitrogen $0.602 \text{ mol dm}^{-3}$; hydrogen $0.420 \text{ mol dm}^{-3}$ and ammonia $0.113 \text{ mol dm}^{-3}$. What is value of K_c .

Solution

The equilibrium concentrations are

$$[\text{N}_2] = 0.602 \text{ mol dm}^{-3}; \quad [\text{H}_2] = 0.420 \text{ mol dm}^{-3}; \quad \text{and} \quad [\text{NH}_3] = 0.113 \text{ mol dm}^{-3}.$$

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

Now put the equilibrium concentration values in the equilibrium expression

$$K_c = \frac{[0.113]^2}{[0.602][0.420]^3} = 0.286 \text{ mol}^{-2} \text{ dm}^6$$

Problem 9.3

For a reaction between PCl_3 and Cl_2 to form PCl_5 , the equilibrium constant is $0.13 \text{ mol}^{-1} \text{ dm}^3$ at a particular temperature. When the equilibrium concentrations of PCl_3 and Cl_2 are 10.0 and 9.0 mol dm^{-3} , respectively. What is the equilibrium concentration of PCl_5 ?

Solution

$$[\text{PCl}_3] = 10 \text{ mol dm}^{-3} \qquad [\text{Cl}_2] = 9.0 \text{ mol dm}^{-3}$$

$$K_c = 0.13 \text{ mol}^{-1} \text{ dm}^3 \qquad [\text{PCl}_5] = ?$$

Now write the balanced chemical equation and equilibrium constant expression



$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

Now put the known values in above equation and rearrange

$$0.13 = \frac{[\text{PCl}_5]}{(10.0)(9.0)}$$

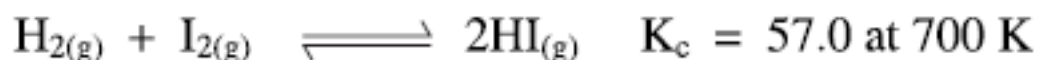
$$[\text{PCl}_5] = 0.13 \times 10.0 \times 9.0 = 11.7 \text{ mol}^{-1} \text{ dm}^3$$

9.4 IMPORTANCE OF EQUILIBRIUM CONSTANT

Knowing the numerical value of equilibrium constant of a chemical reaction, direction as well as extent of the reaction can be predicted.

1. Predicting Direction of a Reaction

Direction of a reaction at a particular moment can be predicted by inserting the concentration of the reactants and products at that particular moment in the equilibrium expression. Consider the gaseous reaction of hydrogen with iodine.



We withdraw the samples from the reaction mixture and determine the concentrations of $\text{H}_{2(g)}$, $\text{I}_{2(g)}$ and $\text{HI}_{(g)}$. Suppose concentrations of the components of the mixture are:

$$[\text{H}_2]_t = 0.10 \text{ mol dm}^{-3} \quad [\text{I}_2]_t = 0.20 \text{ mol dm}^{-3} \quad \text{and} \quad [\text{HI}]_t = 0.40 \text{ mol dm}^{-3}.$$

The subscript 't' with the concentration symbols means that the concentrations are measured at some time t, not necessarily at equilibrium. When we put these concentrations into the equilibrium constant expression, we obtain a value called the reaction quotient Q_c . The reaction quotient for this reaction is calculated as:

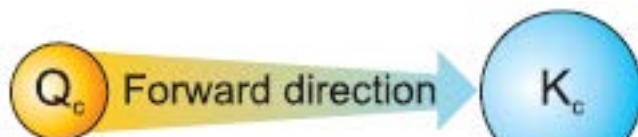
$$Q_c = \frac{[\text{HI}]_t^2}{[\text{H}_2]_t [\text{I}_2]_t} = \frac{(0.40)^2}{(0.10)(0.20)} = 8.0$$

As the numerical value of Q_c (8.0) is less than K_c (57.0), the reaction is not at equilibrium. It requires more concentration of product. Therefore, reaction will move in the forward direction.

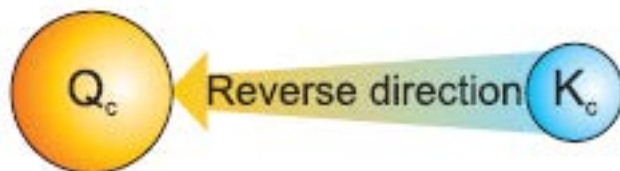
The reaction quotient Q_c is useful because it predicts the direction of the reaction by comparing the value of Q_c with K_c .

Thus, we can make the following generalization about the direction of the reaction.

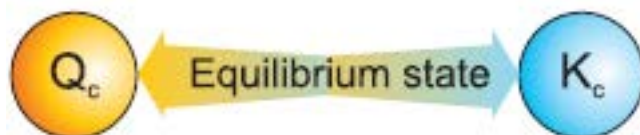
If $Q_c < K_c$; the reaction goes from left to right, i.e., in forward direction to attain equilibrium.



If $Q_c > K_c$; the reaction goes from right to left, i.e., in reverse direction to attain equilibrium.



If $Q_c = K_c$; forward and reverse reactions take place at equal rates i.e., equilibrium has been attained.



(ii) Predicting Extent of a Reaction

Numerical value of the equilibrium constant predicts the extent of a reaction. It indicates to which extent reactants are converted to products. In fact, it measures how far a reaction proceeds before establishing equilibrium state. In general, there are three possibilities of predicting extent of reactions as explained below.

(a) **Large numerical value of K_c :** The large value of K_c indicates that at equilibrium position the reaction mixture consists of almost all products and reactants are negligible. The reaction has almost gone to completion. For example, oxidation of carbon monoxide goes to completion at 1000 K.

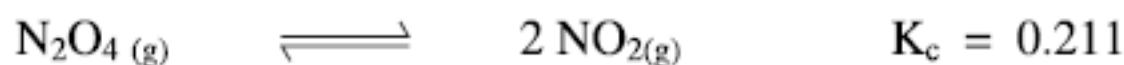


(b) **Small numerical value of K_c :** When the K_c value of reaction is small, it indicates that the equilibrium has established with a very small conversion of reactants to products. At equilibrium position, almost all reactants are present but amount of products is negligible. *Such type of reactions never go to completion.*

For example;



(c) **Numerical value of K_c is neither small nor large.** Such reactions have comparable amounts of reactants and products at equilibrium position. For example:



It indicates that the rates of decomposition of N_2O_4 and combination of NO_2 to form N_2O_4 are almost comparable to each other.



1. What do you mean by the extent of a reaction?
2. Why the reversible reactions do not go to completion?
3. If a reaction has large value of K_c , will it go to completion and why?
4. Which types of reactions do not go to completion?
5. Why the reaction mixture does not have 50% reactants and 50% products at equilibrium position?



Use of atmospheric gases in the manufacture of chemicals.

The two major components of atmosphere are nitrogen and oxygen gases. Both of these gases constitute 99% of the atmosphere.

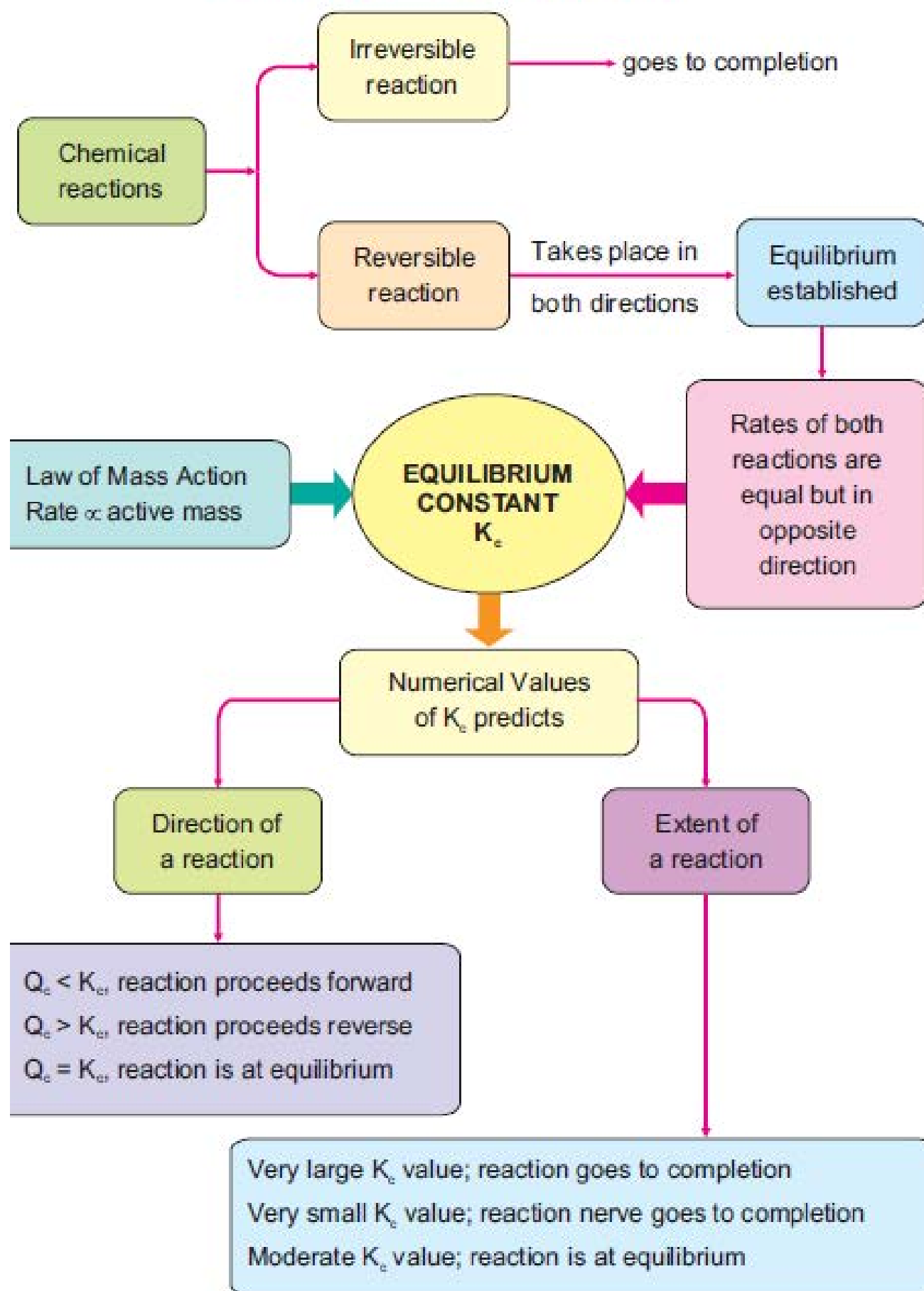
These gases are being used to manufacture chemicals since the advent of 20th century. Nitrogen is used to prepare ammonia, which is further used to manufacture nitrogenous fertilizers.

Oxygen is used to prepare sulphur dioxide which is further used to manufacture king of chemicals sulphuric acid.

Key Points

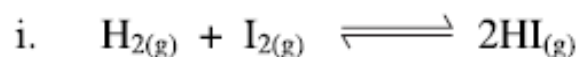
1. Reversible reactions are those in which products recombine to form reactants. These reactions never complete. They proceed in both ways; i.e., forward and reverse.
2. Dynamic equilibrium state is one at which forward and reverse reactions proceed at equal rate but in opposite directions so that overall reaction does not stop.
3. Equilibrium constant K_c is a ratio of the product of concentration of products raised to the power of coefficients to the product of concentration of reactants raised to the power of coefficients as expressed in the balanced chemical equation.
4. Equilibrium constant has no units when number of moles of reactants and products are same.
5. By knowing the value of equilibrium constants, the extent of a reaction can be predicted.
6. Reactions having large K_c value, proceed almost to completion.
7. Reactions having small magnitude of K_c indicates that equilibrium state has established consuming small amount of reactants. Therefore, they never go to completion.
8. Reactions having moderate magnitude have comparable amounts of reactants and products at equilibrium state.

CONCEPT DIAGRAM



Short Questions

1. What are irreversible reactions? Give a few characteristics of them?
2. Define chemical equilibrium state.
3. Give the characteristics of reversible reaction.
4. How is dynamic equilibrium established?
5. Why at equilibrium state reaction does not stop?
6. Why is equilibrium state attainable from either way?
7. What is relationship between active mass and rate of reaction?
8. Derive equilibrium constant expression for the synthesis of ammonia from nitrogen and hydrogen.
9. Write the equilibrium constant expression for the following reactions:



10. How direction of a reaction can be predicted?
11. How can you know that a reaction has achieved an equilibrium state?
12. What are the characteristics of a reaction that establishes equilibrium state at once?
13. If reaction quotient Q_c of a reaction is more than K_c , what will be the direction of the reaction?
14. An industry was established based upon a reversible reaction. It failed to achieve products on commercial level. Can you point out the basic reasons of its failure being a chemist?

Extensive Questions

1. Describe a reversible reaction with the help of an example and graph.
2. Write down the macroscopic characteristics of dynamic equilibrium.
3. State the law of Mass Action and derive the expression for equilibrium constant for a general reaction.
4. What is the importance of equilibrium constant?

Numericals

1. For the decomposition of dinitrogen oxide (N_2O) into nitrogen and oxygen reversible reaction takes place as follows



The concentration of N_2O , N_2 and O_2 are 1.1 mol dm^{-3} , 3.90 mol dm^{-3} and 1.95 mol dm^{-3} respectively at equilibrium. Find out K_c for this reaction.

2. Hydrogen iodide decomposes to form hydrogen and iodine. If the equilibrium concentration of HI is $0.078 \text{ mol dm}^{-3}$, H_2 and I_2 is same $0.011 \text{ mol dm}^{-3}$. Calculate the equilibrium constant value for this reversible reaction:

3. For the fixation of nitrogen following reaction takes place:



When the reaction takes place at 1500 K , the K_c for this is 1.1×10^{-5} . If equilibrium concentrations of nitrogen and oxygen are $1.7 \times 10^{-3} \text{ mol dm}^{-3}$ and $6.4 \times 10^{-3} \text{ mol dm}^{-3}$, respectively, how much NO is formed?

4. When nitrogen reacts with hydrogen to form ammonia, the equilibrium mixture contains 0.31 mol dm^{-3} and 0.50 mol dm^{-3} of nitrogen and hydrogen, respectively. If the K_c is $0.50 \text{ mol}^{-2} \text{ dm}^6$, what is the equilibrium concentration of ammonia?