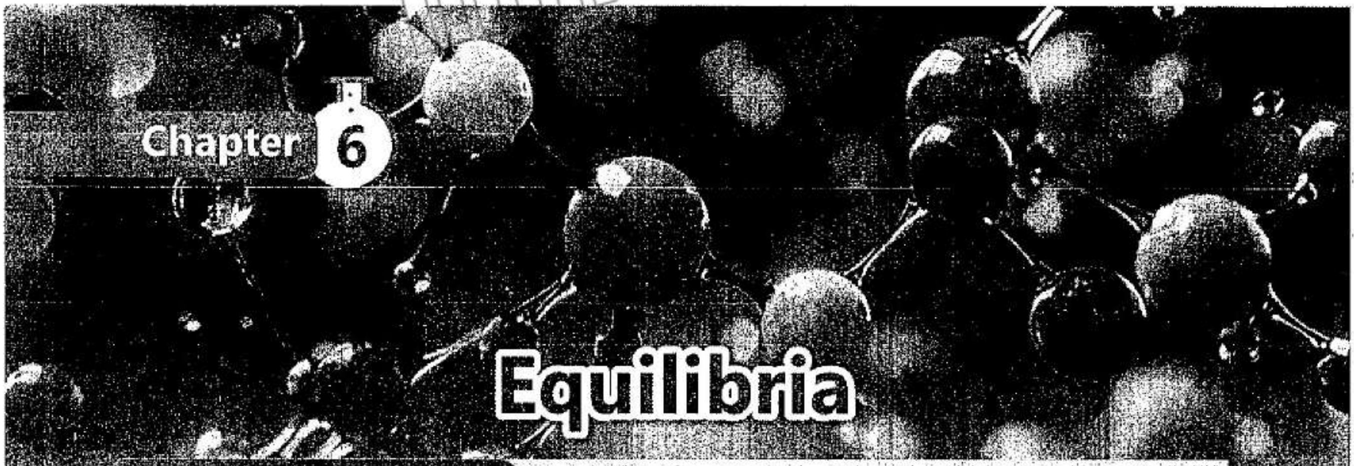

Chapter 6

Equilibria

Student Learning Outcomes

After studying this chapter, students will be able to:

- Recognize that reversible reactions are shown by symbol and may not go to completion
- Describe how changing the physical conditions of a chemical equilibrium system can redirect reversible reactions (Some examples can include: **a.** effect of heat on hydrated compounds **b.** addition of water to anhydrous substances in particular copper (II) sulfate and cobalt (II) chloride
- State that reversible reactions can achieve equilibrium in a closed system when rate of forward and backward reactions are equal.

Introduction

In a chemical reaction, the reactants react to give the products. The reaction will continue until all the reactants or one of the reactants is converted into product. For example, the following reaction takes place immediately in an aqueous solution to give the products.

$$NaCl_{(aq)} + AgNO_{3(aq)} \longrightarrow AgCl_{(s)} + NaNO_{3(aq)}$$

The reaction goes to completion and if stoichiometric amounts of the reactants are used then no reactant species are present at the end of the reaction. Such a reaction is called an irreversible reaction. It moves in the forward direction only.

In the majority of chemical reactions, however, the reaction does not go to completion. The products of the reaction react among themselves to give back the reactants under the same conditions.. Such a reaction moves in both the forward and backward directions under the same conditions. The reactants react to give the products and the products, in turn, react to give back the reactants. The reaction is called a reversible reaction and it is denoted by a double arrow ⇒.

For example,

$$N_{2(g)} + 3H_{2(g)} \underset{Fe}{\overset{400°C,\ 200\ atm}{\rightleftharpoons}} 2NH_{3(g)}$$

In this reaction, one mole of nitrogen gas reacts with three moles of hydrogen gas under the conditions of reaction in a closed container to give two moles of ammonia gas. After its formation, the ammonia gas decomposes to give the reactants back. The reaction never goes to completion. At any time, all the three species are simultaneously present in the reaction mixture.

A reversible reaction, however, goes to completion if either one of the products is withdrawn from the reaction mixture or being a gas, it escapes into the atmosphere. For example, calcium carbonate is decomposed by heating at a particular temperature.

$$CaCO_3(s) \xrightleftharpoons{\text{Heat}} CaO(s) + CO_2(g)$$

If the above reaction is carried out in an open container, the carbon dioxide gas will escape into the atmosphere as soon as it is formed and the reaction is forced to go to completion. If, on the other hand, the reaction is performed in a closed container, the carbon dioxide will react with calcium oxide to give back the reactants.

Like chemical changes, physical changes may also be reversible in nature. Copper sulphate pentahydrate ($CuSO_4$ $5H_2O$) is an important salt which is blue in colour. When this salt is heated strongly, its colour changes to white. This physical change involves the following equilibrium.

$$\underset{\textbf{Hydrated Copper sulphate}}{CuSO_4\ 5H_2O} \xrightleftharpoons{\text{Heat}} \underset{\textbf{Anhydrous Copper sulphate}}{CuSO_4} + 5H_2O$$

When white anhydrous copper sulphate absorbs moisture from the atmosphere, it will turn blue again.

Similar to this, when cobalt chloride hexahydrate ($CoCl_2$ $6H_2O$), which is pink in colour, is heated it is converted to anhydrous $CoCl_2$ which is blue in colour.

$$\underset{\textbf{Hydrated Cobalt chloride (Pink)}}{CoCl_2\ 6H_2O} \xrightleftharpoons{\text{Heat}} \underset{\textbf{Anhydrous Cobalt chloride (Blue)}}{CoCl_2} + 6H_2O$$

In the reverse reaction, the anhydrous cobalt chloride absorbs less moisture, it is first converted into a dihydrate which is purple in colour. This dihydrate then further absorbs four more water molecules to become a hexahydrate which is pink in colour.

$$CoCl_2 \xrightleftharpoons{\text{Limited moisture}} CoCl_2 \cdot 2H_2O \xrightleftharpoons{\text{Moisture}} CoCl_2 \cdot 6H_2O$$

Anhydrous Cobalt chloride (Blue) — **Cobalt chloride dihydrate (Purple)** — **Cobalt hexahydrate (Pink)**

Activity

Take a few grams of blue coloured copper sulphate in a dry test tube. First heat it gently and then strongly for some time.
Note down the observation. Let the test tube cool down. Again note down the observation.

6.1 Dynamic Equilibrium

If a reversible reaction is started by mixing the reactants, the reaction moves in the forward direction only. After some time when enough concentrations of the products are built up, they react to give back the reactants in the reverse reaction.

The reaction will keep on going in both the directions until the rate of forward reaction becomes equal to the rate of reverse reaction. In other words, the number of reactant molecules which will disappear as a result of forward reaction becomes equal to the number of reactant molecules which will form as a result of the reverse reaction. The same will be true for the product molecules. At this stage, the reaction is said to be in a state of chemical equilibrium. It appears as if nothing is going on in the reaction vessel as the concentrations of both reactant and product molecules do not undergo any change at this stage. Since the reaction did not cease at this state of equilibrium, rather it keeps on going in both the directions, this state is called dynamic equilibrium. The concentrations of reacting species (reactants and products) remain constant at equilibrium.

Interesting Information!

Vast deposits of coal are available in Thar, Sindh. This coal can be used to generate electricity. When coal is made to react with steam, CO and H_2 are produced. These products then react by a reversible reaction called catalytic methanation to yield methane.

$$C_{(s)} + H_2O_{(g)} \longrightarrow \underbrace{CO_{(g)} + H_{2(g)}}_{\text{Water gas}}$$

$$CO_{(g)} + 3H_{2(g)} \xrightleftharpoons{\text{Catalyst}} CH_{4(g)} + H_2O_{(g)}$$

Exercise

1. Elaborate an example of dynamic equilibrium which exists in this world between the three physical states of water.
2. Dinitrogen tetra oxide (N_2O_4) is a colourless gas. It slowly changes to brown coloured nitrogen dioxide (NO_2) at 100° C. Predict how the colour of the mixture will change if N_2O_4 is kept in a sealed flask at 100°C.

$$\underset{\textbf{Colourless}}{N_2O_4} \xrightleftharpoons{100^\circ C} \underset{\textbf{Brown}}{2NO_2(g)}$$

The time a reaction will take to attain the state of dynamic chemical equilibrium depends upon the nature of the reaction and the conditions at which the given reversible reaction is performed.

For a dynamic equilibrium to be set up, the rate of the forward reaction must be equal to the rate of backward reaction. This does not happen instantly and for very slow reaction, it may take years. Both the rates of formation and the decomposition of ammonia are reasonably fast at around 400°C in the presence of a catalyst. This reaction will reach the equilibrium state within minutes of the start of reaction.

For example, the following equilibrium reaction takes 4 – 5 seconds to reach at the point of equilibrium.

$$2H_2O_{(l)} \xrightleftharpoons{\text{Electric current}} 2H_{2(g)} + O_{2(g)}$$

6.2 Changing the Physical Conditions of a Chemical Reaction

If a given reversible reaction has attained the state of dynamic equilibrium, it will remain in this state for infinite time unless it is somehow disturbed. A reversible chemical system may be distributed in the following possible ways.

1. Adding or withdrawing one or more of the reacting species
2. Adding or withdrawing one or more of the product species
3. Changing the temperature of the reaction
4. Effect of the presence of a catalyst on a reversible reaction
5. Changing the pressure of the reaction if it involves reactants or the products in the gaseous state

Consider the following reversible reaction at equilibrium.

$$N_{2(g)} + 3H_{2(g)} \underset{\textbf{Catalyst}}{\overset{\textbf{400°C}}{\rightleftharpoons}} 2NH_{3(g)}$$

The concentrations of all the participating chemicals will be constant at the state of equilibrium. At this stage if we add more N_2 gas in the mixture, its concentration will increase and the reaction will no longer maintain its state of equilibrium. To restore the equilibrium state again, nitrogen will react with hydrogen to produce more ammonia. This change will go on until a new state of equilibrium is reached at which the concentration of all the species will again become constant. These new concentrations will, however, be different from the concentrations of the earlier equilibrium state.

Now let us disturb the equilibrium again by withdrawing some of the ammonia gas formed. As a result, its concentration will decrease. To restore the equilibrium state, more nitrogen and hydrogen will react to produce ammonia. When the state of equilibrium is reached again, the concentrations of all the species shall again become constant.

6.3 Effect of Changing the Temperature on the State of Equilibrium

The formation of ammonia is exothermic in the forward direction and hence this reaction will be endothermic in the reverse direction.

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{\text{Heat}} 2\,NH_{3(g)} \quad \Delta H = -92.4 \text{ kJ/mole}$$

If this reaction is at equilibrium and its temperature is increased, the state of the equilibrium will be disturbed again. The ΔH of this reaction is negative. This means the total energy of the system containing N_2 and H_2 is higher than that of ammonia. The increase in temperature of this reaction at equilibrium will push the reaction in the backward direction i.e. the reactants side. Decreasing the temperature will drive the equilibrium to the forward direction.

Effect of Change of Pressure on the Reaction at Equilibrium

Change of pressure will disturb the equilibrium state of only those gaseous reactions in which the number of moles of the reacting gases will be different from the number of moles of the gases being produced. Since the formation of ammonia gas meets such a condition, the state of its equilibrium will be disturbed by changing the pressure exerted on the reaction mixture.

$$\underbrace{\underset{\text{1 mole}}{N_{2(g)}} + \underset{\text{3 moles}}{3H_{2(g)}}}_{\text{4 moles}} \rightleftharpoons \underbrace{\underset{\text{2 moles}}{2NH_{3(g)}}}_{\text{2 moles}}$$

In this reaction, 4 moles of reacting gases are producing two moles of product gas. 4 moles of gases at say S.T.P will occupy $4 \times 22.414 = 89.656\ dm^3$ of volume. 2 moles of NH_3 will occupy $2 \times 22.414 = 44.828\ dm^3$ of volume. If this reaction is at equilibrium and the pressure is increased, the equilibrium will be disturbed. To restore this, the reaction will move to that side in which the number of moles are less i.e. forward direction. The formation of ammonia gas is thus favoured at high pressure.

Effect of the Presence of a Catalyst on the Reversible Reaction

At the stage of dynamic equilibrium, the rates of both forward and backward reactions are equal.

A catalyst increases both the rates of forward and back reactions of a reversible reaction. So if a reversible reaction is carried out in the presence of a catalyst it will decrease the time taken by the reaction to attain the state of equilibrium.

Example: Let us consider another example of a reversible reaction at equilibrium. Phosphorous pentachloride decomposes according to the following equation.

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

According to the equation one mole of the gaseous reactant is giving two moles of the product gases. The reaction is an endothermic reaction. Keeping in view the above description of the reaction, answer the following questions.

i. What will happen if the gas mixture is compressed?
ii. What will happen if we add Cl_2 gas to the equilibrium mixture?
iii. What will happen if the temperature of the reaction is increased?

Interesting Information!

Industrial production of ammonia in Haber Process is a very useful application of the phenomenon of chemical equilibrium. Ammonia gas leads to the formation of an important fertilizer urea. The ability of ammonia gas to be converted into its liquid form easily is used to drive the reaction to completion. In this way, practically 100% conversion of N_2 and H_2 to NH_3 is achieved.

Exercise

The preparation of ethyl acetate is commercially very important because it is used as a thinner in paint industry.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH_{(l)}} + \underset{\text{Acetic acid}}{CH_3COOH_{(l)}} \xrightleftharpoons{\text{dil. } H_2SO_4} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_{5(l)}} + H_2O_{(l)}$$

One way to get the better yield of the product ethyl acetate is to remove water from the reaction mixture as soon as it is formed. Suggest a suitable method to withdraw water from the reaction mixture.
(https://www.rochester.edu)

Key Points

1. Majority of chemical reactions are reversible reactions. Reactants react to give the products and the products, in turn, react or decompose to give back the reactants.
2. A reversible reaction never goes to completion. However, it may be forced to go to completion if one or all the products are withdrawn from the reaction mixture as soon as they are formed.
3. Physical changes may also be reversible in nature.
4. A reversible reaction will keep on going in both the directions until the rate of forward reaction becomes equal to the rate of reverse reaction. At this point the reaction is said to be at a state of chemical equilibrium.
5. Since both the forward and reverse reactions keep on going at the state of chemical equilibrium, it is called a dynamic equilibrium. The concentrations of all the reacting species remain constant at equilibrium.
6. The time a reaction takes to attain the state of dynamic equilibrium depends upon the nature of reaction and the conditions at which the reversible reaction is performed.
7. A reversible chemical system may be disturbed either by adding or withdrawing the reactants or the products and by changing the conditions of temperature, pressure and catalyst.

Exercise

1. Tick (✓) the correct answer.

(i) What will happen if the rates of forward and reverse reactions are very high?
  (a) The equilibrium point will reach very soon.
  (b) The equilibrium point will reach very late.
  (c) The reaction will not attain the state of dynamic equilibrium.
  (d) The reaction will be practically irreversible.

(ii) Predict which components of the atmosphere react in the presence of lightening.
  (a) N_2 and H_2O (b) O_2 and H_2O
  (c) CO_2 and O_2 (d) N_2 and O_2

(iii) An inorganic chemist places one mole of PCl_5 in a container A and one mole of each Cl_2 and PCl_3 in container B. Both the containers were sealed and heated to the same temperature to reach the state of equilibrium. Guess about the composition of mixtures in both the containers.
  (a) Both the containers will have the same composition of mixtures.
  (b) Container A will have more concentration of PCl_3 than B.
  (c) Container A will have less concentration of PCl_3 than B.
  (d) Both the containers will have zero concentration of its reactants.

(iv) CaO or lime is used extensively in steel, glass and paper industries. It is produced in an exothermic reversible reaction by the decomposition of lime ($CaCO_3$). Choose the conditions to produce maximum amount of lime.
  (a) Heating at high temperature in a closed vessel
  (b) Heating at high temperature in an open vessel
  (c) Cooling it in a closed vessel
  (d) Cooling it in an open vessel

(v) What condition should be met for the reversible reaction to achieve the state of equilibrium?
  (a) All the reactants should be converted into the products.
  (b) 50% of the reactants should be converted into products.
  (c) The concentration of all the reactants and the product should become constant.
  (d) One of the products should be removed from the reaction mixture.

(vi) Why the gas starts coming out when you open a can of fizzy drink?

(a) Because the solubility of the gas increases

(b) Because the gas is insoluble in water

(c) Because the gas is dissolved under pressure hence it comes out when pressure is decreased

(d) Because the solubility of the gas decreases at high pressure

(vii) The following reaction is performed in an open vessel.

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

How the equilibrium will be affected if you increase the pressure?

(a) The forward reaction will be favoured

(b) The backward reaction will be favoured

(c) No effect on backward reaction

(d) No effect on forward or backward reaction

(viii) When a reaction will become a reversible one?

(a) If the activation energy of the forward reaction is comparable to that of backward reaction

(b) If the activation energy of the forward reaction is higher than that of backward reaction

(c) If the activation energy of the forward reaction is lower than that of backward reaction

(d) If the enthalpy change of both the reactions is zero.

(ix) Is reversible reaction useful for preparing compounds on large scale?

(a) No (b) Yes

(c) They are useful only when equilibrium lies far to the right side

(d) They are useful only when equilibrium lies far to the left side

(x) What will happen to the concentrations of the products if a reversible reaction at equilibrium is not disturbed?

(a) They will remain constant

(b) They will keep on increasing

(c) They will keep on decreasing

(d) They will remain constant for some time and then start decreasing

2. Questions for Short Answers

i. How is dynamic equilibrium different from the static equilibrium?

ii. How the following reversible reaction will be affected if its temperature is increased?

$$2H_2O_{(l)} \xrightleftharpoons{\text{Electricity}} 2H_{2(g)} + O_{2(g)}$$

iii. How can you get the maximum yield in a reversible reaction?
iv. How can you decrease the time to attain the position of equilibrium in a reversible reaction?
v. What is the effect of increasing pressure on the following reaction?

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

3. Constructed Response Questions

I. Why are some reactions irreversible while others are reversible?
ii. Why are combustion reactions generally irreversible?
iii. Can you make an irreversible reaction reversible and vice versa?
iv. How do you know if a reaction is reversible or irreversible?
v. Do the phase changes in water (solid to liquid, liquid to vapour) reversible or irreversible?

4. Descriptive Questions

i. How can you derive the reversible reaction at equilibrium?
   (a) in the forward direction (b) in the backward direction
ii. Explain how the forward and backward reactions change when the system approaches equilibrium.
iii. Describe the effect of a catalyst on the reversible reaction.
iv. How can a reversible reaction be forced to go to completion?
v. How does change in temperature affect the reaction at equilibrium?

5. Investigate

i. Study the effect of heat on hydrated $CuSO_4$. Why does this salt look coloured and why does it lose colour upon heating?
ii. Synthesis of ammonia gas is very important industrially because it is used in the preparation of urea fertilizer. Explain the conditions you will use to get the maximum yield of ammonia.