8. Chemical Equilibrium

Introduction

Irreversible reaction

- Chemical reactions which proceed to **completion** in **one direction** only are known as irreversible reactions.
- In irreversible reactions, reactants are completely converted into products in a certain interval of time. In these reactions, products do not form reactants again.
- It is represented by full headed arrow. (→)
- **Fast** reactions are generally irreversible.
- A dynamic equilibrium state is not possible.
- Law of mass action or le-Chatelier's principle are not applicable.

Examples, $Na + H_2O \rightarrow NaOH + H_2$

$CaO + H_2O \rightarrow Ca(OH)_2$

$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$

Reversible Reaction

- Chemical reactions which proceed in **both directions** forward and backward simultaneously are known as reversible reactions.
- These reactions **never go to completion** but always continue in both directions.
- Reversible reactions are represented by double-headed arrow: (⇌)
- A dynamic equilibrium state is created.
- Law of mass action and Le –Le-Chatelier's principle are applicable.

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

$H_2 + I_2 \rightleftharpoons 2HI$

$2SO_2 + O_2 \rightleftharpoons 2SO_3$

Static and Dynamic equilibrium

- Reversible reactions proceed in both (forward and backward) directions simultaneously. In a reversible reaction a state is achieved at which the rate of forward reaction becomes equal to the rate of backward reaction. This state is referred to as 'chemical equilibrium'.

EXPLANATION

Consider a reversible reaction A + B $\rightleftharpoons$ C + D in which two reactants A and B are allowed to react together.

At the initial stage, the reaction proceeds in the forward direction only because no product is initially present.

As the reaction starts A and B react to form C and D. Now C and D react to each other to produce A and B and the reaction now proceeds in both forward and backward directions but the rate of forward reaction and the rate of backward reaction are different.

Finally, a state is established at which the rate of backward reaction becomes equal to the rate of forward reaction. This state is called 'chemical equilibrium'.

At the equilibrium state, the reaction does not stop. Reactants form products and products again convert into reactants. This process always continues at constant conditions, but with the passage of time, there is no change in the concentration of reactants and products due to the same rate of reaction. At this point, it appears as if the reaction has stopped because we don't see any change in the concentration of reactants and products with time.

Since chemical equilibrium continues and never stops, chemical equilibrium is a dynamic equilibrium.

1. If a system is at equilibrium, the rate of forward to the reverse reaction is:

a. Less b. Equal c. High d. At equilibrium

2. A chemical change is at equilibrium

a. When the rate of forward reaction becomes zero.
b. When the rates of the forward and the backward reaction are both zero.
c. When all of the reactants have been used up.
d. When the rate of forward reaction is equal to the rate of backward reaction.

3. Chemical equilibrium is dynamic in nature because:

a. Equilibrium is maintained rapidly.
b. The concentrations of reactants and products become same at equilibrium.
c. The concentration of reactants and products are constant but different.
d. Both forward and backward reactions occur at all times with same speed.

1. Define equilibrium. 1

2. NO and NO_2 react at 25°C to give N_2O_3 as shown in the equation.
$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g)$ $\Delta H = -7.2 kJmol^{-1}$
The reaction is reversible and reaches equilibrium in a closed system.
Fig. 2.1 shows how the rate of the forward reaction changes with time.
Initially, the rate of the reverse reaction is zero.
Complete Fig. 2.1 to sketch how the rate of the *reverse* reaction changes with time.

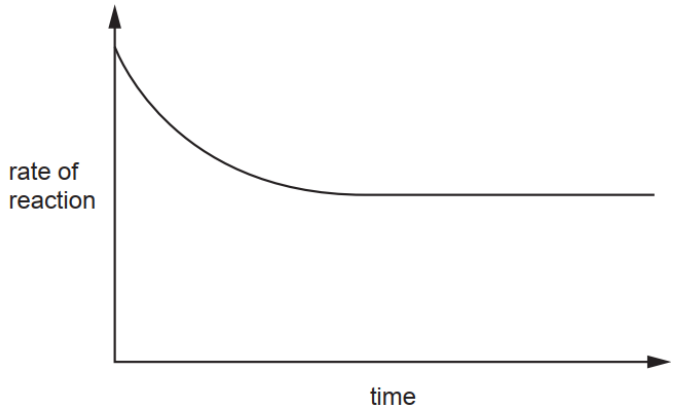

Fig. 2.1

Physical equilibrium

- **Solid – liquid equilibrium**
- **Liquid – Vapour equilibrium etc.**

Characteristics of Chemical Equilibrium

Law of mass action

From many experimental observations, CM Guldberg and P Waage in 1863 proposed a generalization applicable for chemical equilibrium.

Statement: **At a constant temperature and pressure, the rate at which a substance reacts is proportional to its active mass (or concentrations) of all the reactants raised to the powers equal to their stoichiometric coefficients in the balance chemical equation.**

Active mass: is the **molar concentration** of the substance. It is denoted by including the formula of the substance in a square bracket.

Let us consider a general reversible reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

Here A and B are reactants, C and D are products and a, b, c and d are their stoichiometric coefficients respectively.

According to law of mass action,

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

Or, $R_f = K_f [A]^a [B]^b$ ..... (i)

Where k_f is proportionality constant for forward reaction.

Similarly,

Rate of backward reaction, $R_b \propto [C]^c [D]^d$

Or, $R_b = K_b [C]^c [D]^d$ ..... (ii)

Where k_b is proportionality constant for backward reaction.

Here, [A], [B], [C] and [D] are the active masses of the A, B, C and D at the state of equilibrium of the reaction.

Now, at equilibrium,

Rate of forward reaction = Rate of backward reaction

Or, $K_f [A]^a [B]^b = K_b [C]^c [D]^d$

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

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

The constant K_c or K_{eq} is called equilibrium constant.

The equilibrium constant of a reversible reaction is defined as the ratio of the products of the active masses of the products to the products of the active masses of the reactants all rose to the power of their stoichiometric coefficients.

4. The number of gram molecules of a substance present in unit volume is termed as:
   a. Activity
   b. Molar concentration
   c. normal solution
   d. active mass

3. Define law of mass action. 1
4. What is meant by the term active mass? Express the active mass of the reactants in the following reaction; $2P+Q \longrightarrow$ Products. 2
5. Define equilibrium constant. 1
6. **Write equilibrium constant K_c for the reactions:** (1 each)

$I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$ $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$C(s) + CO_2(g) \rightleftharpoons 2\,CO + heat$ $Fe(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

$2\,Cu(NO_3)_2(s) \rightleftharpoons 2\,CuO(s) + 4\,NO_2(g) + O_2(g)$

$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO + 6\,H_2O + heat$

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

$3Fe(s) + 3H_2O(g) \rightleftharpoons Fe_2O_3(s) + 3\,H_2(g)$

7. **Write short notes on law of mass action.** **5**

   (HINT: write the statement, derive the expressions for K_c, and explain the characteristics and significances of equilibrium constant)

8. Write short notes on Law of mass action and characteristics of equilibrium constant. 5
9. Write short notes on Law of mass action and chemical equilibrium. 5
10. Write short notes on Law of mass action and equilibrium constant. 5

Characteristics of Equilibrium constant

The equilibrium in any reversible reaction is characterized by the equilibrium constant. Its value depends upon nature of reaction, temperature and pressure.

1. Equilibrium constant does not depend upon the use of catalyst.
2. Change in concentration of reactants or products do not change the value of equilibrium constant.
3. The equilibrium constant for a particular reaction only depends upon the temperature and if the involved species are gases it depends upon pressure. It's always constant at given temperature and pressure.

Significance of Equilibrium constant

- If value of equilibrium constant is high, it indicates the reaction goes almost to completion in forward direction. Because, K_c is the ratio of K_f/K_b hence higher K_c means higher value of K_f or rate of forward reaction is higher.
- If the value of equilibrium is low, it indicates the reaction does not go towards completion and the yield will be very low.

Unit of equilibrium constant

As equilibrium constant is the ratio between the molar concentrations of product and reactants, if the molar concentration of product and reactants are the same, it has no unit.

5. If the equilibrium constant for a reaction is large, what can be assumed for the reaction?
   a. Very little product is formed.
   b. Very little reactants remain at the equilibrium.
   c. The reaction goes to completion.
   d. Large amount of reactant remain at equilibrium.

6. The rate constant of a reaction depends on:
   a. Temperature
   b. Time of reaction
   c. Initial concentration of reactants
   d. Extent of reaction

11. Why is forward reaction favored when $K_c > 1$? 1
12. **What information would you obtain when equilibrium constant $K_c >$ 1? 1**
13. Why is backward reaction favored when $K_c < 1$? 1

Relation between K_p and K_c

For gaseous equilibrium systems we can use partial pressure of gases instead of molar concentration. Therefore,

"Equilibrium constant determined by using partial pressure of gases in a gaseous chemical equilibrium is denoted by **Kp**"

Consider a general gaseous reversible reaction:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

For the reaction K_p is

$$Kp = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} \qquad (1)$$

Where P_A, P_B, P_C and P_D = partial pressure of gases A, B C and D respectively.

As, $PV = nRT$

Or $P = (n/V)RT$

As, $n/V = C$ = molar concentration

So, $P = CRT$, putting the value of P

$$Kp = \frac{(C_cRT)^c \times (C_DRT)^d}{(C_ART)^a \times (C_BRT)^b} \qquad (2)$$

$$Kp = \frac{[Cc]^c x [C_D]^d}{[C_A]^A x [C_B]^b} X \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$Kp = Kc(RT)^{(c+d)-(a+b)}$$

$$\boxed{\mathbf{Kp = Kc(RT)^{\Delta n}}} \qquad \mathbf{(3)}$$

Δn is the difference in the number of moles of product and reactants. or Δn= (c+d)- (a+b)

From above relation we conclude three results as follows.

I) **Kp = Kc:** In this case there is no change in volume and Δn will be equal to zero. For example:

$H_2 + I_2 \rightleftharpoons 2HI$

In this example volumes of products are equal to the volumes reactants.

2) **Kp > Kc:** In this case reaction occurs with the increase in volume and the value of Δn is more than zero. For example:

$2NH_3 \rightleftharpoons N_2 + 3H_2$

In this example volumes of products are greater than the volumes reactants.

3) **Kp < Kc**: In this case reaction occurs with the decrease in volume and the value of Δn is less than zero. For example:

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

In this example volumes of products are less than the volumes reactants

14. **What is the relationship between K_c and K_p for the following reaction?**

$N_2 + O_2(g) \rightleftharpoons 2NO(g)$ $\quad$ $I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\quad$ $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(g) + heat$ $\qquad (1)$

7. For the reaction $N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) + heat$

a. $K_p = K_c$ c. $K_p = K_cRT$

b. $K_p = K_c(RT)^{-2}$ d. $K_p = K_c(RT)^{-1}$

8. The ratio of Kp to Kc for following the reaction is :

$$NO\ (g) + 1/2\ Cl_2(g) \rightleftharpoons NOCl\ (g)$$

a. $\sqrt{RT}$ c. $1/\ (RT)^2$

b. $(RT)^2$ d. $1/\sqrt{RT}$

9. Kp = Kc is possible in

a. $N_2(g) + H_2(g) \rightleftharpoons NH_3\ (g)$

b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + heat$

c. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

d. $N_2 + O_2(g) \rightleftharpoons 2NO(g)$

10. In which reaction Kp > Kc

a. $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

b. $N_2(g) + H_2(g) \rightleftharpoons NH_3\ (g)$

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

d. $2\ NH_3\ (g) \rightleftharpoons N_2(g) + 3\ H_2(g)$

15. **Write short notes on relation between k_p and k_c.** **4**

16. Write the relation between K_p and K_c. What is the condition for a gaseous reaction to have $K_p=K_c$? 1+1

17. Write a chemical equilibrium in which K_c becomes equal to K_p. 1

le-Chatelier's Principle

Statement: **If a system in equilibrium is subjected to a constraint (stress), the equilibrium shifts in such a direction as to reduce the effect of applied constraint.**

In other words: If a system at equilibrium is disturbed by some change, the system will shift in a direction to minimize or undo the effect of change.

1) The effect of change in concentration:

If at equilibrium state, the concentration of one or more substances present in equilibrium mixture is changed, the equilibrium system will no longer remain in equilibrium state

►On increasing the concentration of reactant, forward reaction will be increased and if the concentration of product is increases, backward reaction proceeds.

►We can say that; if equilibrium is disturbed by increasing concentration, the system will shift in that direction where concentration is decreases. And if equilibrium is disturbed by decreasing concentration, the system will shift in that direction where concentration is increases.

2) The effect of change in temperature

Effect of change in temperature is related to the nature of reaction whether it is an endothermic reaction or an exothermic reaction.

A; For endothermic reaction, K_c increases with the increase in temperature.
B; For exothermic reaction, K_c decreases with the increase in temperature.

►If we disturb the equilibrium by increase in temperature, the system will shift in that direction where heat is absorbed.

►It is important to note that the reverse of exothermic is endothermic and the reverse of endothermic is exothermic.

►Exothermic reaction is favoured by low temperature and endothermic is favoured by high temperature.

3) The effect of change in pressure

Pressure only affects the equilibrium when there is change in volume occurs.

►If we disturb the equilibrium by increase in pressure, the system will shift in that direction to which volume is decreases.

When the volumes of reactants and products are equal there will be no affect of pressure. For example:

$$H_2 + I_2 \rightleftharpoons 2HI$$
1 volume + 1 volume 2 volumes

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

As the volume of product is greater than reactants therefore the yield of ammonia will increase by increasing pressure. At low pressure reverse reaction will proceed.

$$2SO_3 \rightleftharpoons 2SO_2 + O_2$$
2 V 2 V 1 V

The increase in pressure increases the backward direction.

4) Effect of catalyst

Catalysts affect the rate of forward and backward reaction at the same time. Therefore, it does not affect the equilibrium however it reduces the time to reach equilibrium.

11. The factor that affects the position of equilibrium of the reaction
    a. Pressure c. Catalyst
    b. Temperature d. All

12. According to le-Chatelier's principle, adding heat to a solid $\rightleftharpoons$ liquid equilibrium will cause the
    a. Temperature to increase
    b. Temperature to decrease
    c. Amount of liquid to decrease
    d. Amount of solid to decrease

13. In which equilibrium will an increase in pressure at constant temperature increase the yield of the products on the right-hand side of the equation?
    A $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
    B $4HCl(g) + O_2(g) \rightleftharpoons 2H_2O(g) + 2Cl_2(g)$
    C $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
    D $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

14. The Haber process for the manufacture of ammonia is represented by the equation shown.
    $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92$ kJ mol^{-1}
    Which statement is correct about this reaction when the temperature is increased?
    A Both forward and backward rates increase.
    B The backward rate only increases.
    C The forward rate only increases.
    D There is no effect on the backward or forward rates.

15. SO_3 is manufactured from SO_2 and O_2 in the Contact process.
The reaction is exothermic.
Which row shows the effect on the equilibrium yield obtained in the Contact process of increasing the temperature and of adding a vanadium(V) oxide catalyst?

	increasing the temperature	adding vanadium(V) oxide as catalyst
A	equilibrium yield decreases	equilibrium yield increases
B	equilibrium yield decreases	equilibrium yield unchanged
C	equilibrium yield increases	equilibrium yield unchanged
D	equilibrium yield increases	equilibrium yield increases

16. An increase in temperature on the reaction, $N_2 + O_2(g) \rightleftharpoons 2\ NO(g);\ \Delta H = 43.2\ Kcal$ will:

a. Increase the yield of NO
b. Decrease the yield of NO
c. Not affect the yield of NO
d. Not help the reaction to proceed in forward direction

17. The synthesis of ammonia from Nitrogen and Hydrogen proceeds with a decrease in volume, this reaction will be favored by

a. decrease in pressure
b. unaffected by pressure
c. increase in pressure
d. addition of ammonia

18. According to Le- Chatelier's principle, which of the following shift the reaction of Haber's process for formation of NH_3 to right side?

a. concentration of H_2 is decreased
b. pressure is increased
c. temperature is increased
d. pressure is decreased

19. A synthesis for methanol is shown.
$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \quad \Delta H = -49\ kJ\ mol^{-1}$
Which conditions would produce the greatest yield of methanol at equilibrium?

	pressure	temperature / °C
A	high	80
B	high	20
C	low	80
D	low	20

20. Nitrogen dioxide, NO_2, exists in equilibrium with dinitrogen tetroxide, N_2O_4.
$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad H = -57\ kJ\ mol^{-1}$
Which conditions give the greatest percentage of $N_2O_4(g)$ at equilibrium?

	pressure	temperature
A	high	high
B	high	low
C	low	high
D	low	low

21. Nitric acid is produced by oxidising ammonia. The first step is to react ammonia with oxygen in the presence of a catalyst to form nitrogen monoxide.

$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H = -1636$ kJ mol^{-1}

Which set of conditions will produce the greatest yield of nitrogen monoxide at equilibrium?

	TEMPERATURE	PRESSURE
A	HIGH	LOW
B	HIGH	HIGH
C	LOW	HIGH
D	LOW	LOW

23. Hydrogen is produced industrially from methane as shown in the equation.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H^\circ = +205$ kJ mol^{-1}

Which conditions give the highest yield of hydrogen at equilibrium?

	pressure	Temperature
A	low	high
B	high	low
C	high	high
D	low	low

24. Consider the following exothermic reaction where CO (g) is oxidised to CO_2 (g). The optimum conditions to obtain a high yield of CO_2 are;

$$CO\ (g) + 1/2O_2\ (g) \rightleftharpoons CO_2\ (g)$$

a. High T and low P
b. Low T and low P
c. Low T and high P
d. High T and high P

18. State Le-Chatelier's Principle. 1
19. **Write short notes on Le-Chatelier's principle** **5**
20. Write short notes on the Application of Le-Chatelier's Principle in chemical equilibrium. 5
21. Write short notes on the Application of Le-Chatelier's Principle in Physical and chemical equilibrium. 5
22. Write short notes on Le-Chatelier's Principle and its applications. 5

23. **What happens when pressure is increased in the following equilibrium reactions?**

$N_2 + O_2(g) \rightleftharpoons 2NO(g)$ $\quad$ $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$N_2(g) + H_2(g) \rightleftharpoons NH_3(g)$ $\quad$ $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ *2*

24. **Why does pressure have no effect on:**

$I_2(g) + 3H_2(g) \rightleftharpoons 2HI(g)$ *2*

25. **How does temperature change affect the equilibrium of the given reaction?**

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, ΔH=-22.4kJ *2*

26. *Predict the effect of temperature on the equilibrium of the reaction:*

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, ΔH= -93.6 kJ *2*

27. *How do increases in temperature and pressure affect the equilibrium of the following reaction?* $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + heat$ *2*

28. *Why is the formation of SO_3 favoured by increasing pressure and decreasing temperature in the following system?*

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

29. **Mention the proper conditions for maximum yield of SO_3 in the following equilibrium reaction.**

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

30. *What is the effect of an increase of pressure and a decrease in temperature on the following chemical equilibrium?*

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

31. *What is the effect of increasing pressure and decreasing temperature on the following equilibrium:*

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + heat$ *2*

32. *Predict the favourable conditions for the forward reaction in the following case:*

$4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO + 6\ H_2O + heat$ *2*

33. *How does the change in temperature and pressure affect the equilibrium of the following reaction?*

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = -93.6$ kJ

4

34. Given following is the reaction for the industrial manufacture of ammonia gas, which is very important for the production of different nitrogenous fertilisers like urea.

$$N_2(g) + 3\,H_2(g) \underset{200\text{-}900\ atm}{\overset{450^oC,\ Fe\text{-}Mo}{\rightleftharpoons}} 2\,NH_3(g) + 92.6\ KJ/mol$$

a. What will be the effect of decreasing pressure in the above equilibrium?
b. Why does the equilibrium shift in the backwards direction upon increasing the temperature of the above system?

35. ***What would be the effect on the position of equilibrium of the reaction***

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

of
a) adding Cl_2
b) adding PCl_3
c) decreasing the pressure by increasing the volume of the system d) increasing temperature (the reaction is endothermic in the forward reaction)
e) adding a catalyst. ***5***

***** This is not a complete note. It is just to guide you. It is recommended to study the prescribed textbooks along with this material. *****