Unit 8

Physical and chemical equilibrium

Claude Louis Berthollet, a Savoyard-French chemist, studied the mechanism of reversible chemical reaction and developed the theory of chemical equilibria. He also contributed to modern chemical nomenclature. He was the first to demonstrate the bleaching action of chlorine gas, and developed a solution of sodium hypochlorite that acts as a bleaching agent.

Learning Objectives

After studying this unit, the students will be able to

• describe the meaning of equilibrium

• explain the dynamic nature of equilibrium involved in physical and chemical processes

• state the law of mass action

• deduce the expression for equilibrium constants, K_C and K_P

• establish the relationship between K_P and K_C

• predict the extent of reaction using equilibrium constant

• state Le-Chatelier's principle

• explain the effect of various factors that affect a system at equilibrium.

• derive Van't Hoff equation.

8.1 Introduction

In our daily life, we observe several chemical and physical changes. For example, a banana gets ripened after few days, silver gets tarnished in few months and iron gets rusted slowly. These processes proceed in one direction. Now let us consider the transport of oxygen by hemoglobin in our body as an illustration for a reversible change. The hemoglobin combines with oxygen in lungs to form oxyhemoglobin. The oxy-hemoglobin has a tendency to form hemoglobin by

releasing oxygen. In fact, in our lungs all the three species coexist.

Few chemical reactions proceed in only one direction whereas many reactions proceed in both the directions and these reactions are called reversible reactions.

In chemical reactions, the concentration of the reactants decreases and that of the products increases with time. In reversible reactions, initially the reaction proceeds towards the formation of the product. Upon formation of the product, the reverse reaction begins to take place. At a particular stage, the rate of the reverse reaction is equal to that of the forward reaction indicating a state of equilibrium.

It is desirable to know the three crucial aspects of chemical reactions namely the feasibility, the rate of the reaction and the extent of reaction. We know that the feasibility of a reaction is given by thermodynamics. Chemical kinetics will tell about the rate of the reaction. The equilibrium constant tells about the extent of a reaction which we will discuss in this chapter. We will also discuss the types of equilibrium, the significance of equilibrium constant and its relationship to thermodynamic quantities and the response of chemical equilibrium to change in the reaction conditions.

8.2. Physical and chemical equilibrium:

There are different types of equilibrium. For example, if two persons with same weight sit on opposite sides of a see-saw at equal distance from the fulcrum, then the see-saw will be stationary and straight and it is said to be in equilibrium.
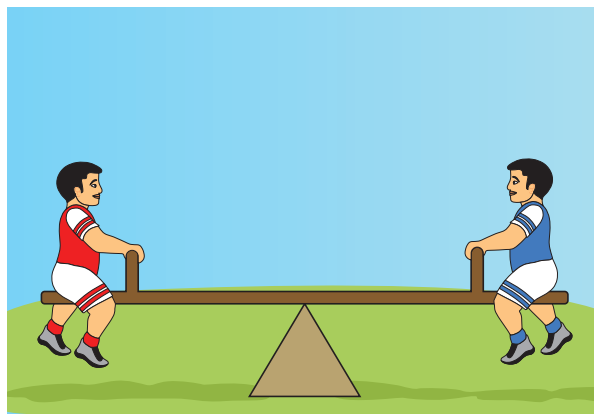
Fig. 8.1 Illustration of equilibrium

Another example of a state of equilibrium is the game of "tug-of-war." In this game a rope is pulled taut between two teams. There may be a situation when both the teams are pulling the rope with equal force and the rope is not moving in either direction. This state is said to be in equilibrium.

Fig. 8.2. Tug-of War

In reversible processes, the rate of two opposing reactions equals at a particular stage. At this stage the concentration of reactants and products do not change with time. This condition is not static and is dynamic, because both the forward and reverse reactions are still occurring with the same rate.

8.2.1 Physical equilibrium

A system in which the amount of matter constituting different phases does not change with time is said to be in physical equilibrium. This involves no perceptible physical change in the system. To understand the physical equilibrium let us analyse the following phase changes.
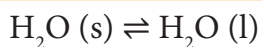
Solid-liquid equilibrium

Let us consider the melting of ice in a closed container at 273 K. This system will reach a state of physical equilibrium in which the amount of water in the solid phase and liquid phase does not change with time. In the process the total number of water molecules leaving from and returning to the solid phase at any instant are equal.

If some ice-cubes and water are placed in a thermos flask (at 273K and 1 atm pressure), then there will be no change in the mass of ice and water.

At equilibrium,

$$\text{Rate of melting of ice} = \text{Rate of freezing of water}$$

$$H_2O \text{ (s)} \rightleftharpoons H_2O \text{ (l)}$$

The above equilibrium exists only at a particular temperature and pressure. The temperature at which the solid and liquid phases of a substance are at equilibrium is called the melting point or freezing point of that substance.

Liquid - Vapour equilibrium

Similarly, there exists an equilibrium between the liquid phase and the vapour phase of a substance. For example, liquid water is in equilibrium with its vapour at 373 K and 1 atm pressure in a closed vessel.

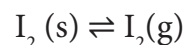$$H_2O \text{ (l)} \rightleftharpoons H_2O \text{ (g)}$$
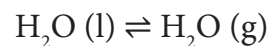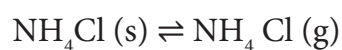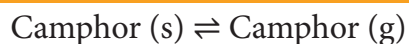
Here
Rate of evaporation = Rate of condensation

The temperature at which the liquid and vapour phases are at equilibrium is called the boiling point and condensation point of the liquid.

Solid - Vapour equilibrium

Consider a system in which the solid sublimes to vapour. In this process also, equilibrium can be established between these two phases. When solid iodine is placed in a closed transparent vessel, after sometime, the vessel gets filled up with violet vapour due to sublimation of iodine. Initially, the intensity of the violet colour increases, after sometime it decreases and finally it becomes constant, as the following equilibrium is attained.

$$I_2 \text{ (s)} \rightleftharpoons I_2 \text{(g)}$$

More examples

$$\text{Camphor (s)} \rightleftharpoons \text{Camphor (g)}$$
$$NH_4Cl \text{ (s)} \rightleftharpoons NH_4Cl \text{ (g)}$$

8.2.2 Equilibrium involving dissolution of solids or gases in liquids

Solid in liquids

When you add sugar to water at a particular temperature, it dissolves to form sugar solution. If you continue to

add much sugar, you will reach a stage at which the added sugar remains as solid and the resulting solution is called a saturated solution. Here, as in the previous cases a dynamic equilibrium is established between the solute molecules in the solid phase and in the solution phase.

$$\text{Sugar (Solid)} \rightleftharpoons \text{Sugar (Solution)}$$
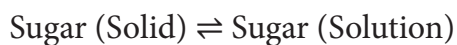
In this process

$$\text{Rate of dissolution of solute} = \text{Rate of crystallisation of solute}$$

Gas in liquids

When a gas dissolves in a liquid under a given pressure, there will be an equilibrium between gas molecules in the gaseous state and those dissolved in the liquid.
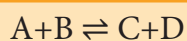
Example:

In carbonated beverages the following equilibrium exists.

$$CO_2 \text{ (g)} \rightleftharpoons CO_2 \text{ (Solution)}$$

Henry's law is used to explain such gas-solution equilibrium processes.

8.3. Chemical Equilibrium

Similar to physical processes chemical reactions gradually attain a state of equilibrium after sometime. Let us consider a general reversible reaction.

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

Initially only A and B are present.

Soon, a few molecules of the products C and D are formed by the forward reaction. As the concentration of the products increases, more products collide and react in the backward direction. This leads to an increase in the rate of backward reaction. As the rate of reverse reaction increases, the rate of the forward reaction decreases. Eventually, the rate of both reactions becomes equal.
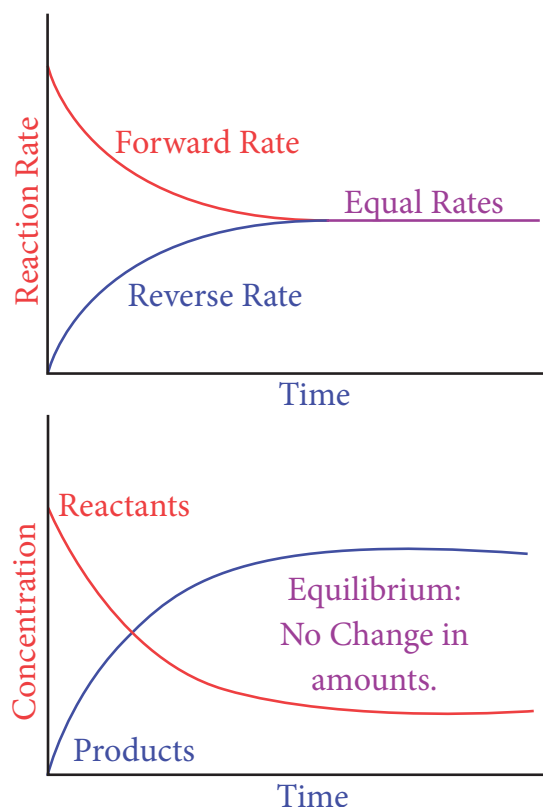

Figure: 8.3 Attainment of equilibrium state for the variation of the rates of forward and backward reactions with time.

8.4. Dynamic nature of equilibrium:

Let us consider, a situation in multi storey building, people are moving from first floor to second floor and vice versa. Assume that a certain number people moves up from first floor to second floor in a specific time, and the same number of people moves down from second floor to the first floor in the same time. Now, the rate of movement of people from first to second floor equals the

rate of movement of people from second to first floor, and hence the number of people in each floor will remain the same. Thus the population of people on the two floors is in a dynamic equilibrium Let us extend this analogy to understand dynamic nature of equilibrium.

Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.

For example,

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2HI \text{ (g)}$$

8.5 Homogeneous and heterogeneous equilibria

8.5.1 Homogeneous equilibrium

In a homogeneous equilibrium, all the reactants and products are in the same phase.

For example:

$$H_2 \text{ (g)} + I_2 \text{ (g)} \rightleftharpoons 2HI \text{ (g)}$$

In the above equilibrium, H_2, I_2 and HI are in the gaseous state.

Similarly, for the following reaction, all the reactants and products are in homogeneous solution phase.

$$CH_3COOCH_3(aq)+H_2O(aq)$$
$$\updownarrow$$
$$CH_3COOH(aq)+CH_3OH \text{ (aq)}$$
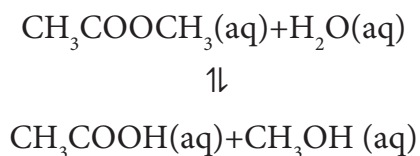
8.5.2 Heterogeneous equilibrium

If the reactants and products of a reaction in equilibrium, are in different phases, then it is called as heterogeneous equilibrium.

Example:

$$H_2O \text{ (l)} \rightleftharpoons H_2O \text{ (g)}$$
$$CaCO_3 \text{ (s)} \rightleftharpoons CaO \text{ (s)} + CO_2 \text{ (g)}$$
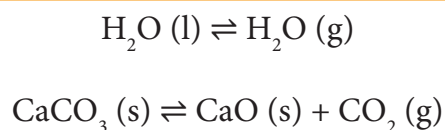
8.6 Law of mass action

In 1864 two Norwegian chemists namely Maximilian Guldberg and Peter Waage formulated the law of mass action, based on the experimental studies of many reversible reactions. The law states that,

"At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".
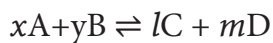
$$\text{Rate } \alpha \text{ [Reactant]}^x$$

where, x is the stoichiometric coefficient of the reactant and the square bracket represents the active mass (concentration) of the reactants.

$$\text{Active mass} = \left(\frac{n}{V}\right) \text{ mol dm}^{-3}\text{(or) mol L}^{-1}$$

where n is the number of moles and V is the volume of the container (dm³ or L)

8.6.1 Equilibrium constants (K_p and K_C):

Let us consider a reversible reaction,

$$xA + yB \rightleftharpoons lC + mD$$

where, A and B are the reactants, C and D are the products and x, y, l and m are the stoichiometric coefficients of A, B, C and D, respectively.

Applying the law of mass action, the rate of the forward reaction,

$$r_f \, \alpha \, [A]^x [B]^y \text{ (or) } r_f = k_f [A]^x [B]^y$$

Similarly, the rate of the backward reaction,

$$r_b \, \alpha \, [C]^l [D]^m$$
$$\text{(or)}$$
$$r_b = k_b [C]^l [D]^m$$

where k_f and k_b are proportionality constants

At equilibrium,

Rate of forward reaction (r_f)

= Rate of backward reaction (r_b)

$$k_f [A]^x [B]^y = k_b [C]^l [D]^m$$

or $\quad \dfrac{k_f}{k_b} = \dfrac{[C]^l [D]^m}{[A]^x [B]^y} = K_c$

where, K_c is the equilibrium constant in terms of concentration (active mass).

At a given temperature, the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants is a constant, known as equilibrium constant. Later when we study chemical kinetics we will learn that this is only approximately true.
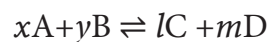
If the reactants and products of the above reaction are in gas phase, then the equilibrium constant can be written in terms of partial pressures as indicated below,

$$k_p = \frac{p_C^l \times p_D^m}{p_A^x \times p_B^y}$$

Where, p_A, p_B, p_C, and p_D are the partial pressures of the gas A, B, C and D, respectively.

8.6.2 Relation between K_p and K_c

Let us consider the general reaction in which all reactants and products are ideal gases.

$$xA + yB \rightleftharpoons lC + mD$$

The equilibrium constant, K_c is

$$k_c = \frac{[C]^l [D]^m}{[A]^x [B]^y} \qquad (1)$$

and K_p is,

$$k_p = \frac{p_C^l \times p_D^m}{p_A^x \times p_B^y} \qquad (2)$$

The ideal gas equation is

$$PV = nRT$$

or

$$P = \frac{n}{V}RT$$

Since

Active mass = molar concentration = n/V

P = active mass × RT

Based on the above expression the partial pressure of the reactants and products can be expressed as,

$$p_A^x = [A]^x [RT]^x$$

$$p_B^y = [B]^y [RT]^y$$

$$p_C^l = [C]^l [RT]^l$$

$$p_D^m = [D]^m [RT]^m$$

On substitution in Eqn. 2,

$$k_p = \frac{[C]^l [RT]^l [D]^m [RT]^m}{[A]^x [RT]^x [B]^y [RT]^y} \qquad (3)$$

$$k_p = \frac{[C]^l [D]^m [RT]^{l+m}}{[A]^x [B]^y [RT]^{x+y}}$$

$$k_p = \frac{[C]^l [D]^m}{[A]^x [B]^y} [RT]^{(l+m)-(x+y)} \qquad (4)$$

By comparing equation (1) and (4), we get

$$k_p = K_c (RT)^{(\Delta n_g)} \qquad (5)$$

where,

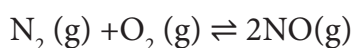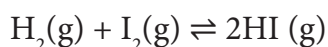Δn_g is the difference between the sum of number of moles of products and the sum of number of moles of reactants in the gas phase.

The following relations become immediately obvious.

When $\Delta n_g = 0$

$$K_p = K_c (RT)^0 = K_c$$

Example:

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

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

When $\Delta n_g = +ve$

$$K_p = K_c (RT)^{+ve}$$

$$K_p > K_c$$

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

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

When $\Delta n_g = -ve$

$$K_p = K_c (RT)^{-ve}$$

$$K_p < K_c$$

Example:

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O (g)$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3 (g)$$
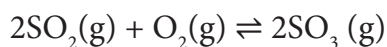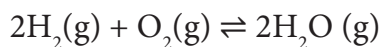
Table 8.1 Relation between equilibrium constants for some reversible reactions

Reversible reactions	Equilibrium constant
For the forward reaction *x A+yB $\rightleftharpoons$ lC+mD*	K_c

If the reaction is reversed, $lC + mB \rightleftharpoons xA + yB$	$K_c^{'} = \dfrac{1}{K_c}$
$A \overset{K_1}{\rightleftharpoons} B$ $\quad B \overset{K_2}{\rightleftharpoons} C$ $C \overset{K_3}{\rightleftharpoons} D$ $\quad A \overset{K_4}{\rightleftharpoons} D$	$K_4 = K_1 K_2 K_3$

8.6.3 Equilibrium constants for heterogeneous equilibrium

Consider the following heterogeneous equilibrium.

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

The equilibrium constant for the above reaction can be written as

$$k_c = \frac{[CaO(s)][CO_2(g)]}{CaCO_3 \text{ (s)}}$$

A pure solid always has the same concentration at a given temperature, as it does not expand to fill its container. i.e. it has same number of moles L^{-1} of its volume. Therefore, the concentration of a pure solid is a constant. The above expression can be modified as follows
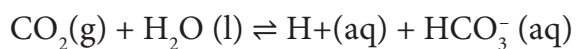
$$K_c = [CO_2 \text{ (g)}]$$

or

$$K_p = p_{CO_2}$$

The equilibrium constant for the above reaction depends only the concentration of carbon dioxide and not the calcium carbonate or calcium oxide. Similarly, the active mass (concentration) of the pure liquid does not change at a given temperature. Consequently, the concentration terms of pure liquids can also be excluded from the expression of the equilibrium constant.
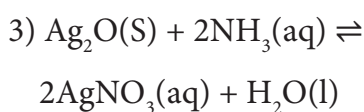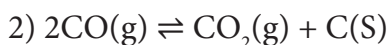
For example,

$$CO_2(g) + H_2O \text{ (l)} \rightleftharpoons H+(aq) + HCO_3^- \text{ (aq)}$$

Since, H_2O (l) is a pure liquid the Kc can be expressed as

8

$$K_C = \frac{[H^+ (aq)][HCO_3^- (aq)]}{[CO_2 (g)]}$$

Example

Write the K_p and K_c for the following reactions

1) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

2) $2CO(g) \rightleftharpoons CO_2(g) + C(S)$

3) $Ag_2O(S) + 2NH_3(aq) \rightleftharpoons$

$\quad 2AgNO_3(aq) + H_2O(l)$
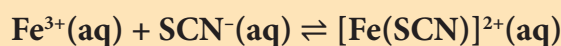
1) $\quad K_C = \dfrac{[SO_3]^2}{[SO_2]^2 [O_2]}$

$\quad K_P = \dfrac{P_{SO_3}^2}{P_{SO_2}^2 \times PO_2}$

2) $\quad \therefore K_C = \dfrac{[CO_2]}{[CO]^2}$ and $K_P = \dfrac{P_{CO_2}}{P_{CO}^2}$

3) $\quad K_C = \dfrac{[AgNO_3]^2}{[NH_3]^2}$

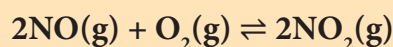# Evaluate Yourself

1) Consider the following reaction

$$\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)}$$

A solution is made with initial Fe^{3+}, SCN^- concentration of 1×10^{-3}M and 8×10^{-4} M respectively. At equilibrium $[Fe(SCN)]^{2+}$ concentration is 2×10^{-4}M. Calculate the value of equilibrium constant.

2) The atmospheric oxidation of NO

$$\mathbf{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)}$$

was studied with initial pressure of 1 atm of NO and 1 atm of O_2. At equilibrium, partial pressure of oxygen is 0.52 atm calculate K_p of the reaction.

8.7 Application of equilibrium constant

The knowledge of equilibrium constant helps us to

1. predict the direction in which the net reaction will take place

2. predict the extent of the reaction and

3. calculate the equilibrium concentrations of the reactants and products.

It is to be noted that these constants do not provide any information regarding the rates of the forward or reverse reactions.

8.7.1 Predicting the extent of a reaction

The value of equilibrium constant, K_c tells us the extent of a reaction, i.e., it indicates how far the reaction has proceeded towards product formation at a given temperature.

A large value of K_c indicates that the reaction reaches equilibrium with high product yield. On the other hand, a low value of K_c indicates that the reaction reaches equilibrium with low product formed. In general, if the K_c is greater than the 10^3, the reaction proceeds nearly to completion. If it is less than 10^{-3}, the reaction rarely proceeds. If the K_c is in the range 10^{-3} to 10^3, significant amount of both reactants and products are present at equilibrium.

Table8.2 Dependence of extent of reaction on Kc

Value of K_C	$K_C < 10^{-3}$	$10^{-3} < K_C < 10^3$	$K_C > 10^3$
Relative concentrations of reactants and products	[Products] << [Reactants]	Significant quantity of Products and Reactants	[Products] >> [Reactants]
Extent of reaction	Reaction makes a little progress in the forward direction	Both the forward and backward reactions reaction make significant progress	Reaction nearly goes to completion
Prediction	Reverse reaction is favoured	Neither forward nor reverse reaction predominates	Forward reaction is favoured
Examples	Decomposition of water at 500 K $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $K_C = 4.1 \times 10^{-48}$ Oxidation of nitrogen at 1000 K $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_C = 1 \times 10^{-30}$	Dissociation of bromine monochloride at 1000 K $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$ $K_C = 5$ Formation HI at 700 K $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K_C = 57.0$	Formation of HCl at 300K $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl (g)$ $K_C = 4 \times 10^{31}$ Oxidation of carbon monoxide at 1000 K $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $K_C = 2.2 \times 10^{22}$

Example

Consider the following equilibrium reactions and relate their equilibrium, constants

i) $N_2 + O_2 \rightleftharpoons 2NO$; K_1

ii) $2NO + O_2 \rightleftharpoons 2NO_2$; K_2

iii) $N_2 + 2O_2 \rightleftharpoons 2NO_2$; K_3

$$K_1 = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$\text{Now } K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$= \frac{[NO_2]^2}{[N_2][O_2]^2} = K_3$$

$$\therefore K_3 = K_1 \times K_2$$

8.7.2 Predicting the direction of a reaction

From the knowledge of equilibrium constant, it is possible to predict the direction in which the net reaction is taking place for a given concentration or partial pressure of reactants and products.

Consider a general homogeneous reversible reaction,

$$xA + yB \rightleftharpoons lC + mD$$
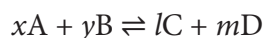
For the above reaction under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.

Under non-equilibrium conditions, the reaction quotient Q can be calculated using the following expression.

$$Q = \frac{[C]^l [D]^m}{[A]^x [B]^y}$$

As the reaction proceeds, there is a continuous change in the concentration of reactants and products and also the Q value until the reaction reaches the equilibrium. At equilibrium Q is equal to K_c at a particular temperature. Once the equilibrium is attained, there is no change in the Q value. By knowing the Q value, we can predict the direction of the reaction by comparing it with Kc.

- If $Q = K_c$, the reaction is in equilibrium state.

- If $Q > K_c$, the reaction will proceed in the reverse direction i.e., formation of reactants.

- If $Q < K_c$, the reaction will proceed in the forward direction i.e., formation of products.

reactants → products   equilibrium   products → reactants
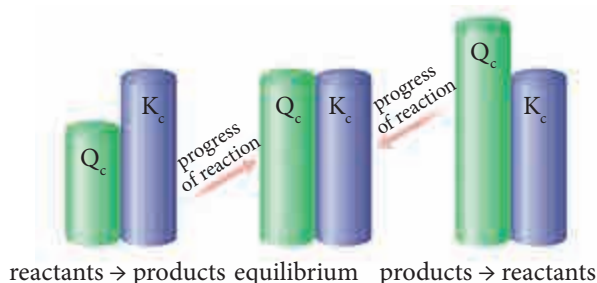
Fig: 8.4 Predicting the direction of a reaction

Example 1

The value of K_c for the following reaction at 717 K is 48.

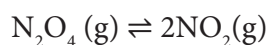$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
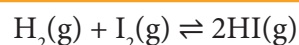
At a particular instant, the concentration of H_2, I_2 and HI are found to be 0.2 mol L^{-1}, 0.2 mol L^{-1} and 0.6 mol L^{-1} respectively. From the above information we can predict the direction of reaction as follows.

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.6 \times 0.6}{0.2 \times 0.2} = 9$$

Since $Q < K_c$, the reaction will proceed in the forward direction.

Example 2

The value of Kc for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Kc = 0.21 at 373 K. The concentrations N_2O_4 and NO_2 are found to be 0.125 mol dm^{-3} and 0.5 mol dm^{-3} respectively at a given time. From the above information we can predict the direction of reaction as follows.

$$Q = \frac{[NO_2]^2}{[N_2O_4]} = \frac{0.5 \times 0.5}{0.125} = 2$$

The Q value is greater than Kc. Hence, the reaction will proceed in the reverse direction until the Q value reaches 0.21

Evaluate Yourself

3) The following water gas shift reaction is an important industrial process for the production of hydrogen gas.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$
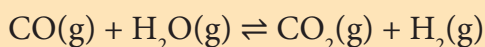
At a given temperature K_p = 2.7. If 0.13 mol of CO, 0.56 mol of water, 0.78 mol of CO_2 and and 0.28 mol of H_2 are introduced into a 2 L flask, and find out in which direction must the reaction proceed to reach equilibrium

8.7.3 Calculation of concentration of reactants and products at equilibrium

If the equilibrium concentrations of reactants and products are known for a reaction, then the equilibrium constant can be calculated and vice versa.

Let us consider the formation of HI in which, 'a' moles of hydrogen and 'b' moles of iodine gas are allowed to react in a container of volume V. Let 'x' moles of each of H_2 and I_2 react together to form 2x moles of HI.

$$H_2(g) + I_{2(g)} \rightleftharpoons 2HI_2(g)$$
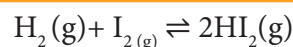
	H_2	I_2	HI
Initial number of moles	a	b	0
number of moles reacted	x	x	0
Number of moles at equilibrium	a-x	b-x	2x
Active mass or molar concentration at equilibrium	$\frac{a\text{-}x}{V}$	$\frac{b\text{-}x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

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

$$= \frac{\left(\dfrac{2x}{V}\right)^2}{\left(\dfrac{a-x}{V}\right)\left(\dfrac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

The equilibrium constant K_p can also be calculated as follows:

We know the relationship between the K_c and K_p

$$K_P = K_C (RT)^{(\Delta n_g)}$$

Here the

$$\Delta n(g) = n_p - n_r = 2 - 2 = 0$$

Hence $K_p = K_c$

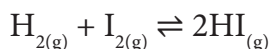$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

Solved Problem

One mole of H_2 and one mole of I_2 are allowed to attain equilibrium. If the equilibrium mixture contains 0.4 mole of HI. Calculate the equilibrium constant.

Given data:

$[H_2] = 1$ mole $[I_2]$ $= 1$ mole

At equilibrium, $[HI] = 0.4$ mole $K_c = ?$

Solution:

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

	H_2	I_2	HI
Initial number of moles	1	1	–
Number of moles at equilibrium	1-x	1-x	2x = 0.4. x=0.2
	0.8	0.8	0.4

$$\therefore K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.4 \times 0.4}{0.8 \times 0.8} = 0.25$$

Dissociation of PCl_5:

Consider that 'a' moles of PCl_5 is taken in a container of volume V. Let 'x' moles of PCl_5 be dissociated into x moles of PCl_3 and x

moles of Cl_2.

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

	PCl_5	PCl_3	Cl_2
Initial number of moles	a	0	0
number of moles dissociated	x	0	0
Number of moles at equilibrium	a-x	x	x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Applying law of mass action,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

The equilibrium constant K_p can also be calculated as follows:

We know the relationship between the K_c and K_p

$$K_p = K_c(RT)^{(\Delta n_g)}$$

Here the

$$\Delta n_g = n_p - n_r = 2 - 1 = 1$$

Hence $K_p = K_c (RT)$

We know that $PV = nRT$

$$RT = \frac{PV}{n}$$

Where n is the total number of moles at equilibrium.
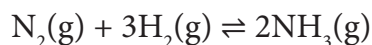
$$n = (a-x) + x + x = (a+x)$$

$$K_p = \frac{x^2}{(a-x)V} \frac{PV}{n}$$

$$K_p = \frac{x^2}{(a-x)V} \frac{PV}{(a+x)}$$

$$K_p = \frac{x^2 P}{(a-x)(a+x)}$$

Synthesis of ammonia:

Let us consider the formation of ammonia in which, 'a' moles nitrogen and 'b' moles hydrogen gas are allowed to react in a container of volume V. Let 'x' moles of nitrogen react with 3x moles of hydrogen to give 2x moles of ammonia.

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

	N_2	H_2	NH_3
Initial number of moles	a	b	0
number of moles reacted	x	3x	0
Number of moles at equilibrium	a-x	b-3x	2x
Active mass or molar concentration at equilibrium	$\frac{a-x}{V}$	$\frac{b-3x}{V}$	$\frac{2x}{V}$

Applying law of mass action,

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

$$= \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$= \frac{\left(\frac{4x^2}{V^2}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$K_C = \frac{4x^2 V^2}{(a-x)(b-3x)^2}$$

The equilibrium constant K_p can also be calculated as follows:

$$K_P = K_C(RT)^{(\Delta n_g)}$$

$$\Delta n_g = n_p - n_r = 2 - 4 = -2$$

$$K_P = \frac{4x^2 V^2}{(a-x)(b-3x)^3}(RT)^{-2}$$

Total number of moles at equilibrium,

n= a-x + b-3x+ 2x = a+b-2x

$$K_P = \frac{4x^2 V^2}{(a-x)(b-3x)^3} \times \left[\frac{PV}{n}\right]^{-2}$$

$$K_P = \frac{4x^2 V^2}{(a-x)(b-3x)^3} \times \left[\frac{n}{PV}\right]^{2}$$

$$K_P = \frac{4x^2 V^2}{(a-x)(b-3x)^3} \times \left[\frac{a+b-2x}{PV}\right]^{2}$$

$$K_P = \frac{4x^2 (a+b-2x)^2}{P^2(a-x)(b-3x)^3}$$

Solved Problems:

1. The equilibrium concentrations of NH_3, N_2 and H_2 are 1.8×10^{-2} M, 1.2×10^{-2} M and 3×10^{-2}M respectively. Calculate the equilibrium constant for the formation of NH_3 from N_2 and H_2. [Hint: M= mol lit^{-1}]

Given data:

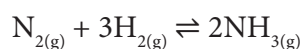$[NH_3] = 1.8 \times 10^{-2}$ M

$[N_2] = 1.2 \times 10^{-2}$ M

$[H_2] = 3 \times 10^{-2}$ M

$K_c = ?$

Solution:

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

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{1.8 \times 10^{-2} \times 1.8 \times 10^{-2}}{1.2 \times 10^{-2} \times 3 \times 10^{-2} \times 3 \times 10^{-2} \times 3 \times 10^{-2}}$$

$$= 1 \times 10^3 \, l^2 \, mol^{-2}$$

2. The equilibrium constant at 298 K for a reaction is 100.
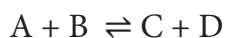
$$A + B \rightleftharpoons C + D$$

If the initial concentration of all the four species is 1 M, the equilibrium concentration of D (in mol lit^{-1}) will be

Given data:

$[A] = [B] = [C] = [D] = 1$ M

$K_c = 100$

$[D]_{eq} = ?$

Solution:

Let x be the no moles of reactants reacted

	A	B	C	D
Initial concentration	1	1	1	1
At equilibrium (as per reaction stoichiometry	1-x	1-x	1+x	1+x

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

$$100 = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$\sqrt{100} = \sqrt{\frac{(1+x)(1+x)}{(1-x)(1-x)}}$$

$$10 = \frac{1+x}{1-x}$$

$$10(1-x) = 1+x$$

$$10 - 10x - 1 - x = 0$$

$$9 - 11x = 0$$

$$11x = 9$$

$$x = \frac{9}{11} = 0.818$$

$[D]$ eq $= 1 + x = 1 + 0.818 = 1.818$ M

Evaluate Yourself

4) 1 mol of PCl$_5$, kept in a closed container of volume 1 dm^3 and was allowed to attain equilibrium at 423 K. Calculate the equilibrium composition of reaction mixture. (The K$_c$ value for PCl$_5$ dissociation at 423 K is 2)

8.8 Le-Chatelier's Principle

Many chemical reactions that have industrial importance such as synthesis of ammonia are reversible in nature. It is important to know the reaction conditions to produce maximum yield. If a system at equilibrium is disturbed by modifying the reaction conditions, then the system adjusts itself the new conditions to re-establish the equilibrium.

The effect of change in reaction conditions such as temperature, pressure and concentration etc… on a system at equilibrium can be predicted by Le Chatelier-Braun principle.

It states that "If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of that disturbance."

8.8. 1 Effect of concentration

At equilibrium, the concentration of the reactants and the products does not change. The addition of more reactants or products to the reacting system at equilibrium causes an increase in their respective concentrations.

According to Le Chatelier's principle, the effect of increase in concentration of a substance is to shift the equilibrium in a direction that consumes the added substance.

Let us consider the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
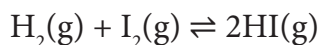
The addition of H_2 or I_2 to the equilibrium mixture, disturbs the equilibrium. In order to minimize the stress, the system shifts the reaction in a direction where H_2 and I_2 are consumed. i.e., the formation of additional HI would balance the effect of added reactant. Hence, the equilibrium shifts to the right (forward direction) i.e. the forward reaction takes place until the equilibrium is re-established. Similarly, removal of HI (product) also favours the forward reaction.

If HI is added to the equilibrium mixture, the concentration HI is increased, and system proceeds in the reverse direction to nullify the effect of increase in concentration of HI .

Let us explain the effect change in concentration by considering the formation of HI from H_2 and I_2. At equilibrium, the concentrations of HI, H_2 and I_2 are 1 M, 0.2 M and 0.1 M respectively.

$$K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{1 \times 1}{0.2 \times 0.1} = 50$$

The equilibrium was disturbed by adding 0.1 M iodine to the reaction mixture. After sometime, the concentration of HI is found to be 1.092 M. Let us verify whether the system proceeds to re-establish the equilibrium according to Le Chatelier's principle.

	H_2	I_2	HI
Concentration at equilibrium	0.2	0.1	1
Disturbance (Addition of 0.1 M iodine)		+0.1	
Concentration immediately after the addition of iodine	0.2	0.2	1
Change in concentration	-x	-x	2x
New concentration	0.2-x	0.2-x	1+2x

Now,

Concentration HI = 1+2x = 1.092 M

2x = 0.092

x = 0.046 M

Therefore, the concentration of hydrogen and iodine at this stage,
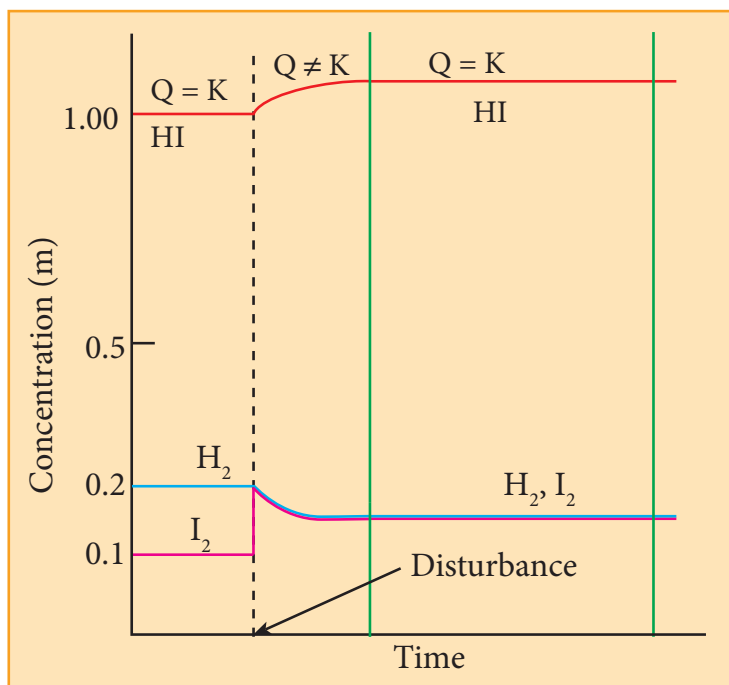
$$[H_2] = 0.2 - X = 0.2 - 0.046 = 0.154$$

$$[I_2] = 0.2 - X = 0.2 - 0.046 = 0.154$$

The reaction quotient Q at this stage,

$$Q = \frac{[HI]^2}{[H_2][I_2]} = \frac{1.096 \times 1.096}{0.154 \times 0.154} \approx 50$$

The Q value is equal to Kc value.

So, we can conclude that the system has reestablished the equilibrium at this stage and the addition of iodine results in the increase in the HI concentration.

Figure 8.5 Effect of addition of iodine on formation of HI

8.8.2 Effect of pressure

The change in pressure has significant effect only on equilibrium systems with gaseous components. When the pressure on the system is increased, the volume decreases proportionately and the system responds by shifting the equilibrium in a direction that has fewer moles of gaseous molecules.

Let us consider the synthesis of ammonia from nitrogen and hydrogen.

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

17
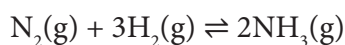
Let the system be allowed to attain equilibrium in a cylinder with a piston. If we press the piston down to increase the pressure, the volume decreases. The system responds to this effect by reducing the number of gas molecules. i.e. it favours the formation of ammonia. If we pull the piston upwards to reduce the pressure, the volume increases. It favours the decomposition of ammonia
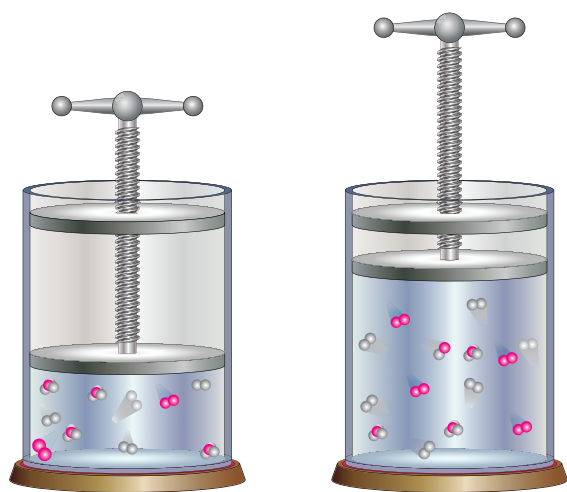
Figure 8.6 Effect of pressure on ammonia synthesis.

However, when the total number of the moles of the gaseous reactants and the gaseous products are equal, the change in pressure has no effect on system at equilibrium.

Let us consider the following reaction
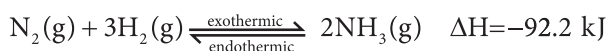
$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
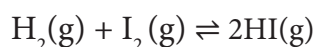
2 moles of reactants $\Rightarrow$ 2 moles of product

Here, the number of moles of reactants and products are equal. So, the pressure has no effect on such equilibrium with $\Delta n_g = 0$.

8.8. 3 Effect of temperature

If the temperature of a system at equilibrium is changed, the system responds by shifting the equilibrium in the direction that attempts to nullify the effect of temperature.

Let us consider the formation of ammonia.

$$N_2(g) + 3H_2(g) \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} 2NH_3(g) \quad \Delta H = -92.2 \text{ kJ}$$

In this equilibrium, the forward reaction is exothermic i.e. the heat is liberated while the reverse reaction is endothermic i.e. the heat is absorbed.

If the temperature of the system is increased (by supplying heat energy), the system responds by decomposing some of the ammonia molecules to nitrogen and hydrogen by absorbing the supplied heat energy. Similarly, the system responds to a drop in the temperature by forming more ammonia molecules from nitrogen and hydrogen, which releases heat energy.

We have already learnt that the change in pressure or concentration causes a change in the equilibrium concentration such that the equilibrium constant remains the same. However, in case of change in temperature, the equilibrium is reestablished with a different equilibrium constant.

8.8.4 Effect of a catalyst

Addition of a catalyst does not affect the state of the equilibrium. The catalyst increases the rate of both the forward and the reverse reactions to the same extent. Hence, it does not change the equilibrium composition of the reaction mixture.

However, it speeds up the attainment of equilibrium by providing a new pathway having a lower activation energy.

For example, in the synthesis of NH_3 by the Haber's process iron is used as a catalyst. Similarly, in the contact process of manufacturing SO_3, platinum or V_2O_5 is used as a catalyst.

8.8.5 Effect of inert gas

When an inert gas (i.e, a gas which does not react with any other species involved in equilibrium) is added to an equilibrium system at constant volume, the total number of moles of gases present in the container increases, that is, the total pressure of gases increases. the partial pressure of the reactants and the products are unchanged. Hence at constant volume, addition of inert gas has no effect on equilibrium.

Table 8.3: Effect of concentration, pressure, temperature, catalyst and Inert gas on equilibrium

Condition	Stress	Direction in which equilibrium shifts
Concentration	Addition of reactants (increase in reactant concentration)	Forward reaction
	Removal of products (decrease in product concentration)	
	Addition of products (increase in product concentration)	Reverse reaction
	Removal of reactants (decrease in reactant concentration)	
Pressure	Increase of pressure (Decrease in volume)	Reaction that favours fewer moles of the gaseous molecules
	Decrease of pressure (Increase in volume)	Reaction that favours more moles of the gaseous molecules
Temperature(Alters equilibrium constants)	Increase (High T)	Towards endothermic reaction
	decrease (Low T)	Towards exothermic reaction
Catalyst (Speeds up the attainment of equilibrium)	Addition of catalyst	No effect
Inert gas	Addition of inert gas at constant volume	No effect

8.9 Van't Hoff Equation

This equation gives the quantitative temperature dependence of equilibrium constant (K). The relation between standard free energy change ($\Delta G°$) and equilibrium constant is

$$\Delta G° = -RT\ln K \qquad (1)$$

We know that

$$\Delta G° = \Delta H° - T\Delta S° \qquad (2)$$

Substituting (1) in equation (2)

$$-RT\ln K = \Delta H° - T\Delta S°$$

Rearranging

$$\ln K = \frac{-\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (3)$$

Differentiating equation (3) with respect to temperature,

$$\frac{d(\ln K)}{dT} = \frac{\Delta H°}{RT^2} \qquad (4)$$

Equation 4 is known as differential form of van't Hoff equation.

On integrating the equation 4, between T_1 and T_2 with their respective equilibrium constants K_1 and K_2.

$$\int_{K_1}^{K_2} d(\ln K) = \frac{\Delta H°}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$[\ln K]_{K_1}^{K_2} = \frac{\Delta H°}{R} \left[-\frac{1}{T}\right]_{T_1}^{T_2}$$

$$\ln K_2 - \ln K_1 = \frac{\Delta H°}{R}\left[-\frac{1}{T_2} + \frac{1}{T_1}\right]$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H°}{R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right] \quad \text{............} (5)$$

Equation 5 is known as integrated form of van't Hoff equation.

Problem:

For an equilibrium reaction K_p = 0.0260 at 25°C ΔH = 32.4 kJmol^{-1}, calculate K_p at 37° C

Solution :

T_1 = 25 + 273 = 298 K

T_2 = 37 + 273 = 310 K

ΔH = 32.4 KJmol^{-1} = 32400 Jmol^{-1}

R = 8.314 JK^{-1} mol^{-1}

K_{p1} = 0.0260

K_{p2} = ?

$$\log \frac{K_2}{K_1} = \frac{\Delta H°}{2.303\,R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

$$\log \frac{K_2}{K_1} = \frac{32400}{2.303 \times 8.314}\left(\frac{310 - 298}{310 \times 298}\right)$$

$$= \frac{32400 \times 12}{2.303 \times 8.314 \times 310 \times 298}$$

$$= 0.2198$$

$$\frac{K_2}{K_1} = \text{anti log } 0.2198 = 1.6588$$

$$K_2 = 1.6588 \times 0.026 = 0.0431$$

Evaluate Yourself

5) The equilibrium constant for the following reaction is 0.15 at 298 K and 1 atm pressure.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g);$$
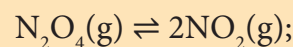
$$\Delta H°_f = 57.32 \text{ KJmol}^{-1}$$

The reaction conditions are altered as follows.

a) The reaction temperature is altered to 100° C keeping the pressure at 1 atm, Calculate the equilibrium constant.

How does oxygen exchanges between maternal and fetal blood in a pregnant women?

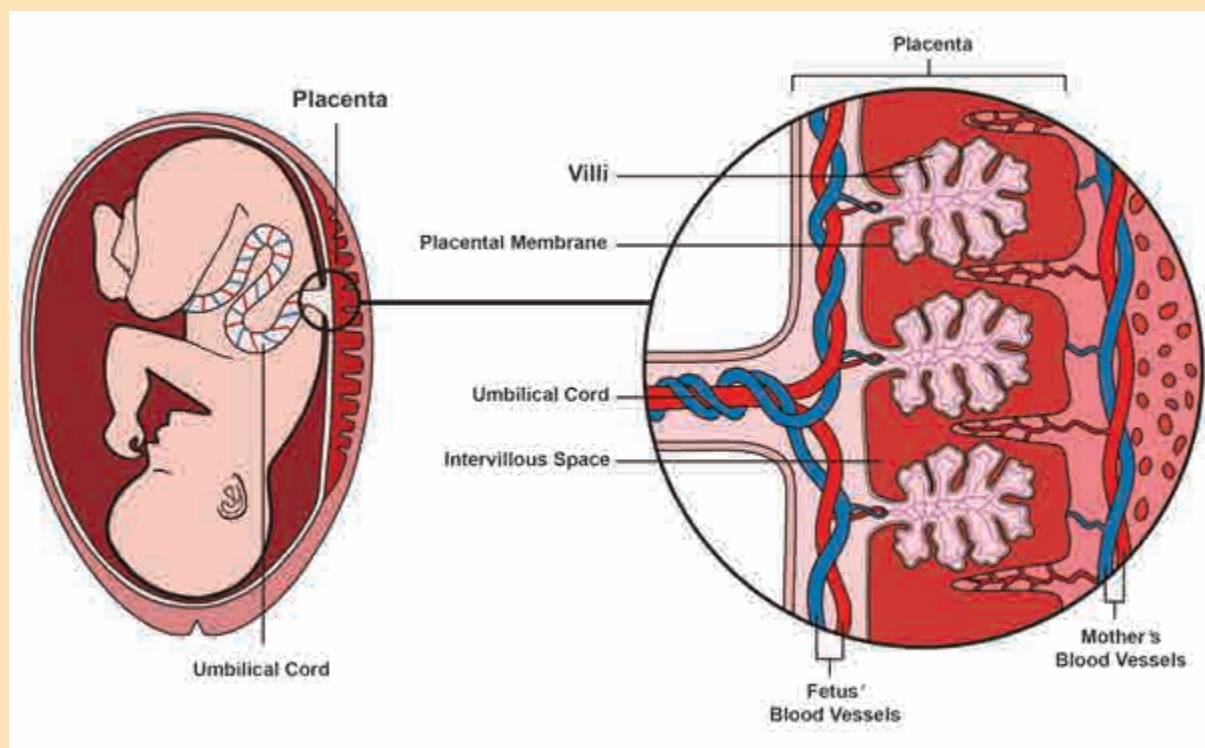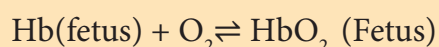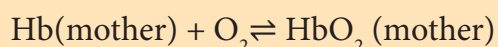In a pregnant women, the oxygen supply for fetus is provided by the maternal blood in the placenta where the blood vessels of both mother and fetus are in close proximity. Both fetal and maternal hemoglobin binds to oxygen reversibly as follows.

$$Hb(mother) + O_2 \rightleftharpoons HbO_2 \text{ (mother)}$$

$$Hb(fetus) + O_2 \rightleftharpoons HbO_2 \text{ (Fetus)}$$

In the above two equilibriums, the equilibrium constant value for the oxygenation of fetal hemoglobin is higher, which is due to its higher affinity for oxygen compared to the adult hemoglobin. Hence in placenta, the oxygen from the mother's blood is effectively transferred to the fetal hemoglobin

SUMMARY

- In our daily life, we observe several chemical and physical changes.

- In some chemical reactions, at a particular stage, the rate of the reverse reaction is equal to that of the forward reaction indicating a state of equilibrium.

There are different types of equilibrium.

Physical equilibrium

Chemical Equilibrium

- Chemical reactions which are reversible do not cease, when equilibrium is attained. At equilibrium the forward and the backward reactions are proceeding at the same rate and no macroscopic change is observed. So chemical equilibrium is in a state of dynamic equilibrium.

- The rate law states that, "At any instant, the rate of a chemical reaction at a given temperature is directly proportional to the product of the active masses of the reactants at that instant".

- The value of equilibrium constant, Kc tells us the extent of a reaction, i.e., it indicates how far the reaction has proceeded towards product formation at a given temperature.

- Under non-equilibrium conditions, reaction quotient 'Q' is defined as the ratio of the product of active masses of reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation to that of the reactants.

- Le-Chatelier's Principle "If a system at equilibrium is disturbed, then the system shifts itself in a direction that nullifies the effect of that disturbance."

- The effect of change in reaction conditions such as temperature, pressure and concentration etc… on a system at equilibrium can be predicted by Le Chatelier-Braun principle.

- vant Hoff equation This equation gives the quantitative temperature dependence of equilibrium constant (K).

Evaluation

1. If K_b and K_f for a reversible reactions are 0.8×10^{-5} and 1.6×10^{-4} respectively, the value of the equilibrium constant is,

   a) 20   b) 0.2×10^{-1}

   c) 0.05   d) none of these

2. At a given temperature and pressure, the equilibrium constant values for the equilibria

   $$3A_2 + B_2 + 2C \xrightleftharpoons{K_1} 2A_3BC \text{ and}$$

   $$A_3BC \xrightleftharpoons{K_2} \frac{3}{2}[A_2] + \frac{1}{2}B_2 + C$$

   The relation between K_1 and K_2 is

   a) $K_1 = \dfrac{1}{\sqrt{K_2}}$ b) $K_2 = K_1^{-\frac{1}{2}}$

   c) $K_1^2 = 2K_2$ d) $\dfrac{K_1}{2} = K_2$

3. The equilibrium constant for a reaction at room temperature is K1 and that at 700 K is K2. If K1 > K2, then

   a) The forward reaction is exothermic

b) The forward reaction is endothermic

c) The reaction does not attain equilibrium

d) The reverse reaction is exothermic

4. The formation of ammonia from $N_2(g)$ and $H_2(g)$ is a reversible reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + Heat
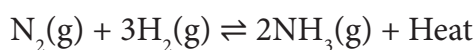
What is the effect of increase of temperature on this equilibrium reaction

a) equilibrium is unaltered

b) formation of ammonia is favoured

c) equilibrium is shifted to the left

d) reaction rate does not change

5. Solubility of carbon dioxide gas in cold water can be increased by

a) increase in pressure

b) decrease in pressure

c) increase in volume

d) none of these

6 Which one of the following is incorrect statement ?

a) for a system at equilibrium, Q is always less than the equilibrium constant

b) equilibrium can be attained from either side of the reaction

c) presence of catalyst affects both the forward reaction and reverse reaction to the same extent

d) Equilibrium constant varied with temperature

7. K_1 and K_2 are the equilibrium constants for the reactions respectively.

$$N_2(g) + O_2(g) \xrightarrow{K_1} 2NO(g)$$

$$2NO(g) + O_2(g) \xrightarrow{K_2} 2NO_2(g)$$
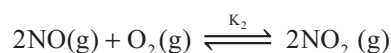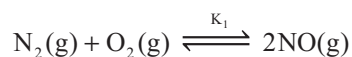
What is the equilibrium constant for the reaction $NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$

a) $\dfrac{1}{\sqrt{K_1 K_2}}$

b) $(K_1 = K_2)^{\frac{1}{2}}$

c) $\dfrac{1}{2K_1 K_2}$

d) $\left(\dfrac{1}{K_1 K_2}\right)^{\frac{3}{2}}$

8. In the equilibrium,

$$2A(g) \rightleftharpoons 2B(g) + C_2(g)$$

the equilibrium concentrations of A, B and C_2 at 400 K are 1×10^{-4} M, 2.0×10^{-3} M, 1.5×10^{-4} M respectively. The value of K_C for the equilibrium at 400 K is

a) 0.06

b) 0.09

c) 0.62

d) 3×10^{-2}

9. An equilibrium constant of 3.2×10^{-6} for a reaction means, the equilibrium is

a) largely towards forward direction

b) largely towards reverse direction

c) never established

d) none of these

10. $\dfrac{K_C}{K_P}$ for the reaction,

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

a) $\dfrac{1}{RT}$

b) $\sqrt{RT}$

c) RT

d) $(RT)^2$

11. For the reaction AB (g) $\rightleftharpoons$ A(g) + B(g), at equilibrium, AB is 20% dissociated at a total pressure of P, The equilibrium

constant K_p is related to the total pressure by the expression

a) $P = 24\, K_p$ b) $P = 8\, K_p$

c) $24\, P = K_p$ d) none of these

12. In which of the following equilibrium, K_p and K_c are not equal?

a) $2\, NO(g) \rightleftharpoons N_2(g) + O_2(g)$

b) $SO_2(g) + NO_2 \rightleftharpoons SO_3(g) + NO(g)$

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

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

13. If x is the fraction of PCl_5 dissociated at equilibrium in the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

then starting with 0.5 mole of PCl_5, the total number of moles of reactants and products at equilibrium is
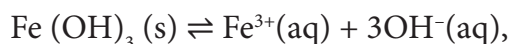
a) $0.5 - x$ b) $x + 0.5$

c) $2x + 0.5$ d) $x + 1$

14. The values of K_{P_1} and K_{P_2} for the reactions

$$X \rightleftharpoons Y + Z$$

$A \rightleftharpoons 2B$ are in the ratio 9 : 1 if degree of dissociation and initial concentration of X and A be equal then total pressure at equilibrium P_1, and P_2 are in the ratio

a) 36 : 1   b) 1 : 1

c) 3 : 1   d) 1 : 9

15. In the reaction,

$$Fe\,(OH)_3\,(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq),$$

if the concentration of OH^- ions is decreased by ¼ times, then the equilibrium concentration of Fe^{3+} will

a) not changed

b) also decreased by ¼ times

c) increase by 4 times

d) increase by 64 times

16. Consider the reaction where $K_p = 0.5$ at a particular temperature

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

if the three gases are mixed in a container so that the partial pressure of each gas is initially 1 atm, then which one of the following is true

a) more PCl_3 will be produced

b) more Cl_2 will be produced

c) more PCl_5 will be produced

d) none of these

17. Equimolar concentrations of H_2 and I_2 are heated to equilibrium in a 1 litre flask. What percentage of initial concentration of H_2 has reacted at equilibrium if rate constant for both forward and reverse reactions are equal

a) 33%   b) 66%

c) $(33)^2\,\%$ d) 16.5 %

18. In a chemical equilibrium, the rate constant for the forward reaction is 2.5×10^2 and the equilibrium constant is 50. The rate constant for the reverse reaction is,

a) 11.5   b) 5

c) 2×10^2 d) 2×10^{-3}

19. Which of the following is not a general

characteristic of equilibrium involving physical process

a) Equilibrium is possible only in a closed system at a given temperature

b) The opposing processes occur at the same rate and there is a dynamic but stable condition

c) All the physical processes stop at equilibrium

d) All measurable properties of the system remains constant

20. For the formation of Two moles of $SO_3(g)$ from SO_2 and O_2, the equilibrium constant is K_1. The equilibrium constant for the dissociation of one mole of SO_3 into SO_2 and O_2 is

a) $\dfrac{1}{K_1}$ b) K_1^2

c) $\left(\dfrac{1}{K_1}\right)^{1/2}$ d) $\dfrac{K_1}{2}$

21. Match the equilibria with the corresponding conditions,

i) Liquid $\rightleftharpoons$ Vapour

ii) Solid $\rightleftharpoons$ Liquid

iii) Solid $\rightleftharpoons$ Vapour

iv) Solute (s) $\rightleftharpoons$ Solute (Solution)

1) melting point

2) Saturated solution

3) Boiling point

4) Sublimation point

5) Unsaturated solution

	(i)	(ii)	(iii)	(iv)
(a)	1	2	3	4
(b)	3	1	4	2
(c)	2	1	3	4
(d)	3	2	4	5

22. Consider the following reversible reaction at equilibrium, A + B $\rightleftharpoons$ C, If the concentration of the reactants A and B are doubled, then the equilibrium constant will

a) be doubled   b) become one fourth

c) be halved   d) remain the same

23. $[Co(H_2O)_6]^{2+}$ (aq) (pink) + $4Cl^-$ (aq) $\rightleftharpoons$ $[CoCl_4]^{2-}$ (aq) (blue)+ 6 H_2O (l)
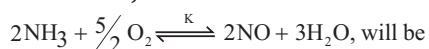
In the above reaction at equilibrium, the reaction mixture is blue in colour at room temperature. On cooling this mixture, it becomes pink in colour. On the basis of this information, which one of the following is true ?

a) $\Delta H > 0$ for the forward reaction

b) $\Delta H = 0$ for the reverse reaction

c) $\Delta H < 0$ for the forward reaction

d) Sign of the ΔH cannot be predicted based on this information.

24. The equilibrium constants of the following reactions are :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1

$N_2 + O_2 \rightleftharpoons 2NO$; K_2

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant (K) for the reaction ;

$2NH_3 + \frac{5}{2}O_2 \overset{K}{\rightleftharpoons} 2NO + 3H_2O$, will be

a) $K_2^3 K_3 / K_1$ b) $K_1 K_3^3 / K_2$

c) $K_2 K_3^3 / K_1$ d) $K_2 K_3 / K_1$

25. A 20 litre container at 400 K contains CO_2 (g) at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value will be :

Given that : $SrCO_3$ (S) $\rightleftharpoons$ SrO (S) + $CO_2(g)$

K_P = 1.6 atm (NEET 2017)

a) 2 litre   b) 5 litre
c) 10 litre   d) 4 litre

26. If there is no change in concentration, why is the equilibrium state considered dynamic ?

27. For a given reaction at a particular temperature, the equilibrium constant has constant value. Is the value of Q also constant ? Explain.

28. What the relation between K_P and K_C. Give one example for which K_P is equal to K_C.

29. For a gaseous homogeneous reaction at equilibrium, number of moles of products are greater than the number of moles of reactants. Is K_C is larger or smaller than K_P.

30. When the numerical value of the reaction quotient (Q) is greater than the equilibrium constant (K), in which direction does the reaction proceed to reach equilibrium ?
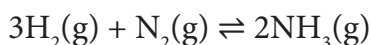
31. For the reaction,

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; ΔH is –ve.

the following molecular scenes represent different reaction mixture (A – green, B – blue)

Closed
←
System
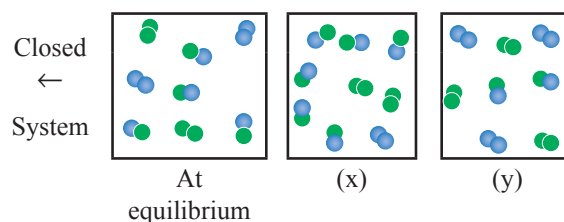
At equilibrium   (x)   (y)

i) Calculate the equilibrium constant K_P and (K_C).

ii) For the reaction mixture represented by scene (x), (y) the reaction proceed in which directions ?

iii) What is the effect of increase in pressure for the mixture at equilibrium.

32. State Le-Chatelier principle.

33. Consider the following reactions,

a) $H_2(g) + I_2(g) \rightleftharpoons 2$ HI

b) $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + $CO_2(g)$

c) $S(s) + 3F_2$ (g) $\rightleftharpoons SF_6$ (g)

In each of the above reaction find out whether you have to increase (or) decrease the volume to increase the yield of the product.

34. State law of mass action.

35. Explain how will you predict the direction of a equilibrium reaction.

36. Derive a general expression for the equilibrium constant K_P and K_C for the reaction

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

37. Write a balanced chemical equation for a equilibrium reaction for which the equilibrium constant is given by expression

$$K_C = \frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$$

38. What is the effect of added inert gas on the reaction at equilibrium.

39. Derive the relation between K_P and K_C.

40. One mole of PCl_5 is heated in one litre closed container. If 0.6 mole of chlorine is found at equilibrium, calculate the value of equilibrium constant.

41. For the reaction

$$SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g),$$

the value of equilibrium constant $K_P = 2.2 \times 10^{-4}$ at 1002 K. Calculate K_C for the reaction.
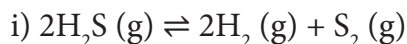
42. To study the decomposition of hydrogen iodide, a student fills an evacuated 3 litre flask with 0.3 mol of HI gas and allows the reaction to proceed at 500 °C. At equilibrium he found the concentration of HI which is equal to 0.05 M. Calculate K_C and K_P.

43. Oxidation of nitrogen monoxide was studied at 200 °C with initial pressures of 1 atm NO and 1 atm of O_2. At equilibrium partial pressure of oxygen is found to be 0.52 atm calculate K_P value.

44. 1 mol of CH_4, 1 mole of CS_2 and 2 mol of H_2S are 2 mol of H_2 are mixed in a 500 ml flask. The equilibrium constant for the reaction $K_C = 4 \times 10^{-2}$ mol^2 lit^{-2}. In which direction will the reaction proceed to reach equilibrium ?

45. At particular temperature $K_C = 4 \times 10^{-2}$ for the reaction

$$H_2S(g) \rightleftharpoons H_2(g) + \frac{1}{2} S_2(g)$$
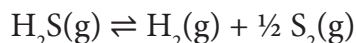
Calculate K_C for each of the following reaction

i) $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

ii) $3H_2S(g) \rightleftharpoons 3H_2(g) + \frac{3}{2} S_2(g)$

46. 28 g of Nitrogen and 6 g of hydrogen were mixed in a 1 litre closed container. At equilibrium 17 g NH_3 was produced. Calculate the weight of nitrogen, hydrogen at equilibrium.

47. The equilibrium for the dissociation of XY_2 is given as,

$$2XY_2(g) \rightleftharpoons 2XY(g) + Y_2(g)$$

if the degree of dissociation x is so small compared to one. Show that

$2 K_p = PX^3$ where P is the total pressure and K_p is the dissociation equilibrium constant of XY_2.

48. A sealed container was filled with 1 mol of $A_2(g)$, 1 mol $B_2(g)$ at 800 K and total pressure 1.00 bar. Calculate the amounts of the components in the mixture at equilibrium given that $K = 1$ for the reaction
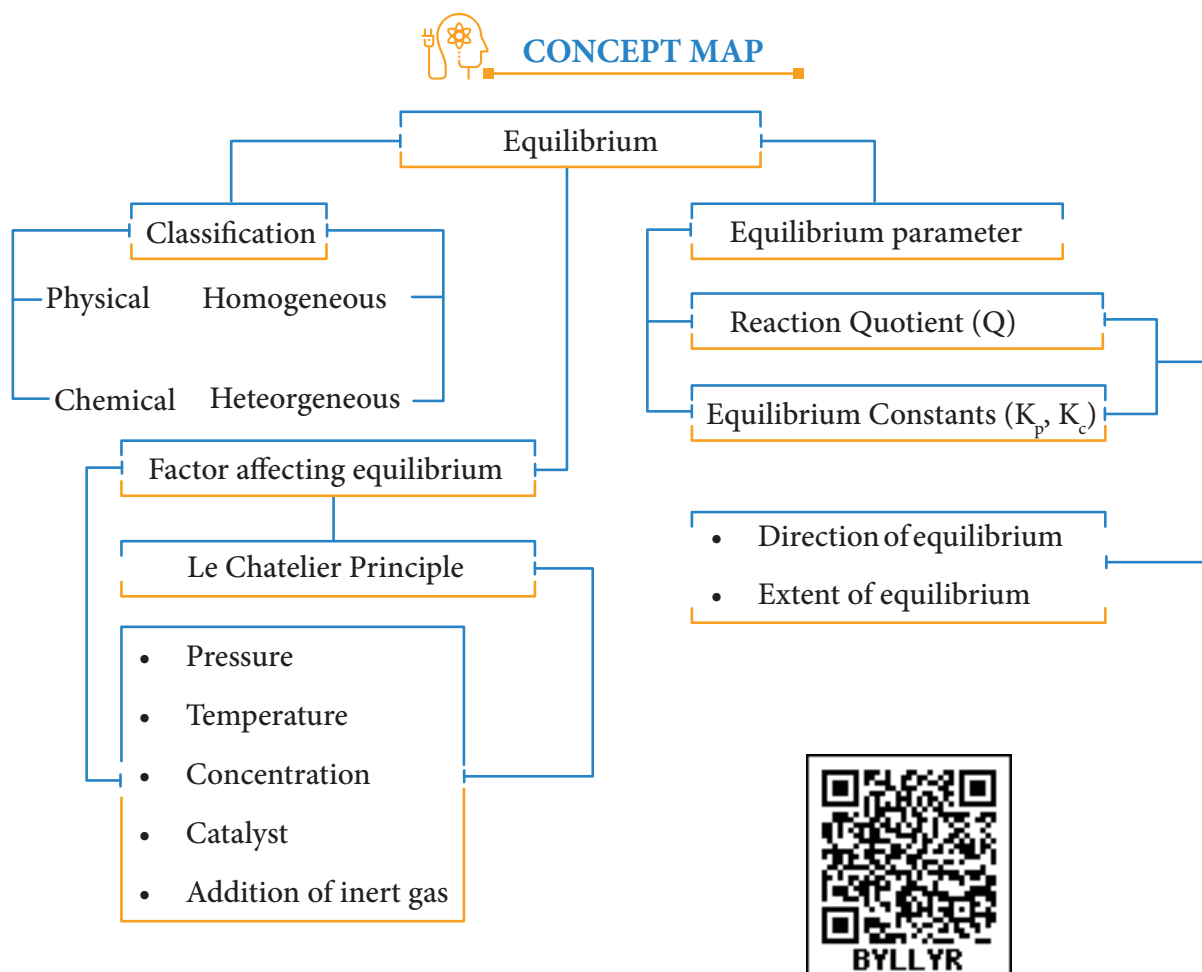
$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

49. Deduce the Vant Hoff equation.

50. The equilibrium constant K_p for the reaction

    $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 8.19×10^2 at 298 K and 4.6×10^{-1} at 498 K. Calculate ΔH^0 for the reaction.

51. The partial pressure of carbon dioxide in the reaction

    $CaCO_3$ (s) $\rightleftharpoons$ CaO (s) + $CO_2(g)$ is 1.017×10^{-3} atm at 500^0 C. Calculate K_p at 600^0c C for the reaction. ΔH for the reaction is 181 KJ mol^{-1} and does not change in the given range of temperature.

CONCEPT MAP

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                          Equilibrium

    Classification                    Equilibrium parameter

  Physical    Homogeneous             Reaction Quotient (Q)

  Chemical    Heteorgeneous           Equilibrium Constants (K_p, K_c)

    Factor affecting equilibrium

       Le Chatelier Principle            • Direction of equilibrium
                                         • Extent of equilibrium
    • Pressure
    • Temperature
    • Concentration
    • Catalyst
    • Addition of inert gas
```

BYLLYR

Effect of temperature and pressure in an equilibrium process

By using this tool, we can determine the effect of pressure and temperature in the equilibrium concentration of the components in ammonia synthesis (Haber process)

Please go to the URL http://www.freezeray.com/ flashFiles/a mmoniaConditions.htm (or) Scan the QR code on the right side

B164_11_CHE_EM

Steps

- Open the Browser and type the URL given (or) Scan the QR Code.

- The website will show the equilibrium reaction involved in ammonia synthesis and the relative concentration of the components. The visual representation and the actual concentration values are given in the box 1.

- Now change the pressure or temperature using the corresponding slider indicated in the box2.

- As you move the slider you will be able to see the change in the equilibrium concentration of reactants and products.

- Now you can understand that if a stress is applied on the system at equilibrium, the system will adjust itself to nullify the effect of the stress.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H \quad -92.4 \text{ kJmol}^{-1}$$

pressure   temperature

3.64 mol   10.92 mol   8.72 mol