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Equilibrium

Mood rings are an interesting example of an equilibrium system. The colour of these rings is said to indicate your mood. However, it actually reads your external body temperature, which may or may not indicate your emotions. The thermotropic liquid crystals fill the ring. As the temperature rises, the liquid crystal substance shifts, giving the ring a dark blue appearance.

Topic Notes

- *Equilibria in Different Processes and Types of Equilibria*
- *Applications of Equilibrium*
- *Acids, Bases, Salts and Ionic Equilibria*
- *Solubility Equilibria*

EQUILIBRIA IN DIFFERENT PROCESSES AND TYPES OF EQUILIBRIA

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TOPIC 1

EQUILIBRIUM IN PHYSICAL PROCESSES

Equilibrium can be better understood if we consider examples of physical processes of phase transformations wherein the physical phases are in equilibrium.

E.g.
Solid ⇌ Liquid
Liquid ⇌ Gas
Solid ⇌ Gas

Solid-Liquid Equilibrium

An example of solid-liquid equilibrium would be ice and water kept in an insulated thermos flask such that there is no exchange of heat between the system and the surroundings. It is observed that the mass of ice and water does not change with time and the temperature remains constant. However, this is a case of dynamic equilibrium due to the constant activity that takes place at the boundary of ice and water.

At equilibrium,

Rate of freezing of water = Rate of melting of ice.

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$$

(Temperature is at 273K and pressure is 1.013 bar)

Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase.

Important

➥ *For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance. Therefore, in the case of ice and water, the normal freezing point of water and the normal melting point of ice is 273 K.*

Liquid-Vapour Equilibrium

At equilibrium the pressure exerted by the water molecules at a given temperature in a closed container remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water); vapour pressure of water increases with temperature. If water undergoes evaporation in a closed container at a given temperature, i.e., it implies that the pressure inside the container increases due to the addition of water molecules in the gaseous state. However, the rate of increase in pressure decreases with time due to the condensation of vapour into water. Subsequently, the equilibrium is attained wherein,

Rate of evaporation = Rate of condensation

$$H_2O_{(l)} \rightleftharpoons H_2O_{(vap)}$$

Important

➥ *For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid. Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitudes, the boiling point decreases.*

Solid-Vapour Equilibrium

If we place solid iodine in a closed vessel after some time the vessel gets filled up with violet vapour and the intensity of colour increases with time. After a certain time, the intensity of colour becomes constant and at this stage, equilibrium is attained. Hence, solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine.

$$I_2\text{ (solid)} \rightleftharpoons I_2\text{ (vapour)}$$

Camphor and NH_4Cl also show this kind of equilibrium.

$$\text{Camphor (solid)} \rightleftharpoons \text{Camphor (vapour)}$$

$$NH_4Cl\text{ (solid)} \rightleftharpoons NH_4Cl\text{ (vapour)}$$

Equilibrium Involving Dissolution of Solids or Gases in Liquids

Solids in liquids

A saturated solution is one where no more solute can be dissolved at a given temperature. In such a saturated solution, a dynamic equilibrium exists between the solute molecules in the solid state and the solution. For example, for saturated sugar solution, the dynamic equilibrium can be written as,

$$\text{Sugar (solid)} \leftrightarrow \text{Sugar (solution)}$$

Also, the rate of dissolution of sugar = rate of crystallisation of sugar.

Important

➥ *Increased temperature increases the solubility of solids in liquids.*

Gases in liquids

Carbon dioxide is soluble in water when higher pressures are applied. In soda cans or soda bottles, the carbon dioxide fizzes out when opened. Inside the closed bottle, there is an equilibrium maintained between the molecules of carbon dioxide in the gaseous state and the molecules dissolved in liquid under pressure. i.e.,

$$CO_2 \text{ (gas)} \rightleftharpoons CO_2 \text{ (solution)}$$

This phenomenon is governed by Henry's Law.

Important

➥ *Henry's Law - The mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.*

$$P = K_H C$$

Where C is the concentration of dissolved gas

K_H is Henry's Law constant

P is the partial pressure of the gas

The value of Henry's law constant of a gas is dependent on the following factors:

(1) The nature of the gas

(2) The nature of the solvent

(3) Temperature and pressure

The nature of the gas and solvent predict whether or not the gas is soluble in the solvent. Non-polar gases are not likely to dissolve in polar solvents and polar gases do not usually dissolve in non-polar solvents. The increased temperature of a liquid decreases the solubility of a gas and the increased pressure increases the same.

General Characteristics of Equilibria Involving Physical Processes

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

(2) Opposing processes occur at the same rate.

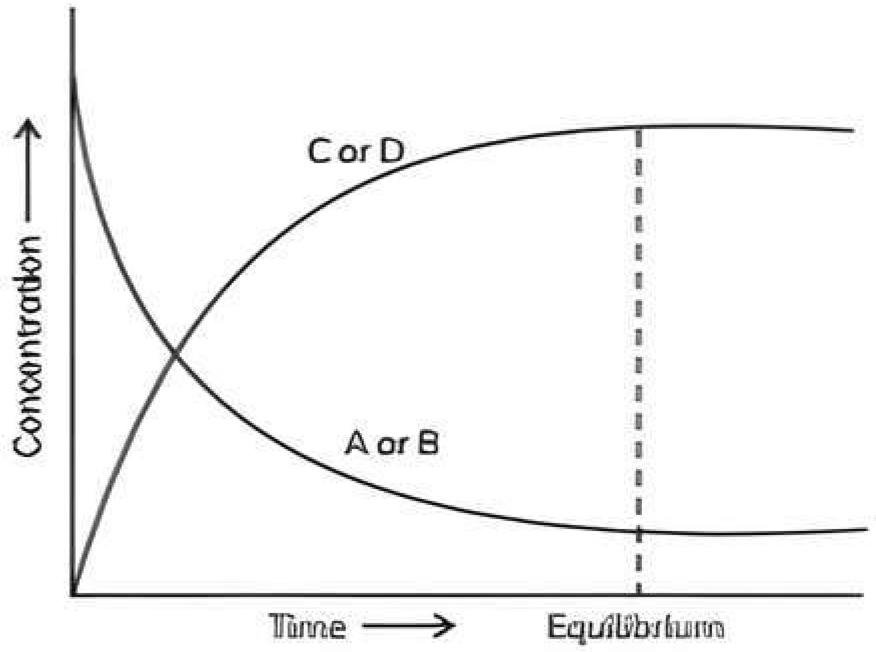
(3) Equilibrium for physical processes is characterised by constant value of one of its parameters at a given temperature. The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

(4) All measurable properties of the system remain constant.

TOPIC 2

EQUILIBRIUM IN CHEMICAL PROCESSES – DYNAMIC EQUILIBRIUM

Chemical reactions can also attain equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is dynamic in nature as it consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

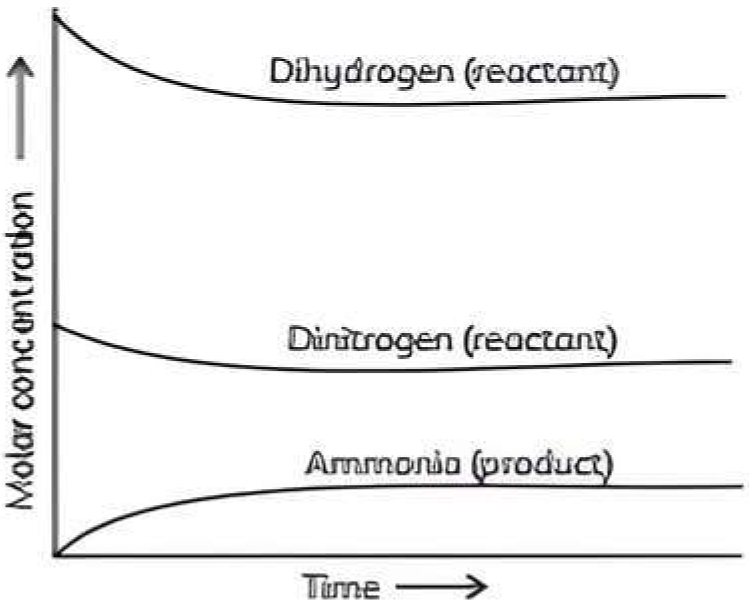


Attainment of chemical equilibrium

Haber's process: The dynamic nature of chemical equilibrium can be demonstrated in the synthesis of ammonia by Haber's process. Haber started with known amounts of dinitrogen and dihydrogen maintained at high temperature and pressure and at regular intervals determined the amount of ammonia present. After a certain time, the composition of the mixture remains the same even though some of the reactants are still present. This constancy in composition indicates that the reaction has reached equilibrium.

In order to understand the dynamic nature of the reaction, synthesis of ammonia is carried out with exactly the same starting conditions (of partial pressure and temperature) but using D_2 (deuterium) in place of H_2. The reaction mixtures starting either with H_2 or D_2 reach equilibrium with the same composition, except that D_2 and ND_3 are present instead of H_2 and NH_3. After equilibrium is attained, these two mixtures (H_2, N_2, NH_3 and D_2, N_2, ND_3) are mixed together and left for a while.

Later, when this mixture is analysed, it is found that the concentration of ammonia is just the same as before. However, when this mixture is analysed by a mass spectrometer, it is found that ammonia and all deuterium-containing forms of ammonia (NH_3, NH_2D, NHD_2 and ND_3) and dihydrogen and its deuterated forms (H_2, HD and D_2) are present. Thus, one can conclude that scrambling of H and D atoms in the molecules must result from a continuation of the forward and reverse reactions in the mixture. If the reaction had simply stopped when they reached equilibrium, then there would have been no mixing of isotopes.



Depiction of equilibrium for the reaction
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3$

The reaction for formation of ammonia in Haber's process:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3$$

Reaction of nitrogen with deuterium:

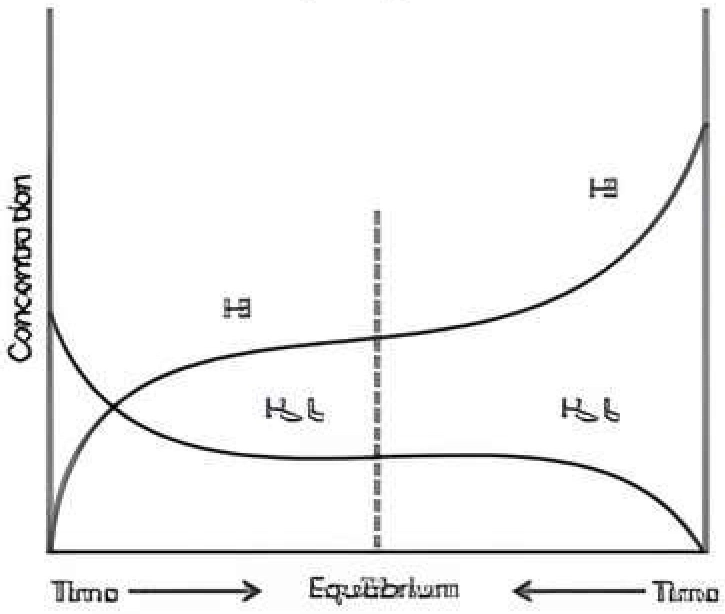
$$N_{2(g)} + 3D_{2(g)} \rightleftharpoons 2ND_3$$

Important

➥ *Chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.*

Let us consider the reaction, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}$. If we start with an equal initial concentration of H_2 and I_2, the reaction proceeds in the forward direction and the concentration of H_2 and I_2 decreases while that of HI increases, until all of these become constant at equilibrium.

We can also start with HI alone and make the reaction to proceed in the reverse direction; the concentration of HI will decrease and the concentration of H_2 and I_2 will increase until they all become constant when equilibrium is reached. If total number of H and I atoms are the same in a given volume, the same equilibrium mixture is obtained whether we start it from pure reactants or pure products.



Chemical equilibrium in the reaction can be attained from either direction

Example 1.1: Case Based:

Mechanical equilibrium is achieved when all particles are at rest and total potential energy of the system is minimum. Thermal equilibrium is result from the absence of temperature gradients in the system and Chemical equilibrium is obtained when no further reaction occurs between reacting substances i.e., forward and reverse rates of reaction are equal. When steam reacts with solid iron, Fe_3O_4 and hydrogen gas are produced. However, the reaction never goes to completion.

(A) Which of the following statements is true for chemical equilibrium?
- (a) All processes stop at chemical equilibrium.
- (b) All particles are at rest at chemical equilibrium.
- (c) Chemical equilibrium is not affected by temperature.
- (d) Chemical equilibrium happens in a closed container.

(B) If a system is at equilibrium, the rate of the forward to the reverse reaction is:
- (a) equal
- (b) less
- (c) high
- (d) rates are unchanged

(C) Give a balanced equation for the reaction between solid iron and steam.

(D) Does the addition of an inert gas change the equilibrium of the above reaction?

(E) Assertion (A): The reaction between solid iron and steam is at a homogeneous equilibrium.

Reason (R): Phase transformation is an example of equilibrium in physical processes.
- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) *(d) Chemical equilibrium happens in a closed container.*

Explanation: The forward and reverse reactions still continue at equilibrium at the same rate. Chemical equilibrium is dynamic in nature which means that the particles are constantly moving. Increasing the temperature changes the position of the equilibrium.

(B) *(a) Equal*

Explanation: At equilibrium, the rate of forward and reverse reactions are equal.

(C) $3Fe_{(s)} + 4H_2O_{(g)} \rightarrow Fe_3O_{4(s)} + 4H_{2(g)}$

(D) No, the addition of inert gas does not change the equilibrium.

(E) *(d) (A) is false but (R) is true.*

Explanation: The reaction between steam and solid iron involves phase transformation which is an example of equilibrium in physical processes. Such types of equilibria are termed as heterogeneous equilibria.

TOPIC 3

LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

A mixture of reactants and products in the equilibrium state is called an equilibrium mixture. The law of chemical equilibrium is simply a mathematical expression which can be derived by the application of the law of mass action to a reversible reaction.

Let us consider a general reversible reaction:

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

Where A and B are the reactants, C and D are the products in the balanced chemical equation. On the basis of experimental studies of many reversible reactions, the Norwegian chemists Cato Maximilian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following equilibrium equation.

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

where K_c is the equilibrium constant and the expression on the right side is called the equilibrium constant expression.

The equilibrium equation is also known as the law of mass action because, in the early days of chemistry, concentration was called "active mass". In order to appreciate their work better, let us consider the reaction between gaseous H_2 and I_2 carried out in a sealed vessel at 731K.

$$\underset{1\ mol}{H_{2(g)}} + \underset{1\ mol}{I_{2(g)}} \rightleftharpoons \underset{2\ mol}{2HI_{(g)}}$$

Six sets of experiments with varying initial conditions were performed, starting with only gaseous H_2 and I_2 in a sealed reaction vessel in the first four experiments (1, 2, 3 and 4) and only HI in the other two experiments (5 and 6). Experiments 1, 2, 3 and 4 were performed taking different concentrations of H_2 and/or I_2, and with time it was observed that the intensity of the purple colour remained constant and equilibrium was attained. Similarly, for experiments 5 and 6, the equilibrium was attained from the opposite direction.

Data obtained from all six sets of experiments are:

Experiment number	Initial concentration/mol L^{-1}			Equilibrium concentration / mol L^{-1}		
	$[H_{2(g)}]$	$[I_{2(g)}]$	$[HI_{(g)}]$	$[H_{2(g)}]$	$[I_{2(g)}]$	$[HI_{(g)}]$
1	2.4×10^{-2}	1.38×10^{-2}	0	1.14×10^{-2}	0.12×10^{-2}	2.52×10^{-2}
2	2.4×10^{-2}	1.68×10^{-2}	0	0.92×10^{-2}	0.20×10^{-2}	2.96×10^{-2}
3	2.44×10^{-2}	1.98×10^{-2}	0	0.77×10^{-2}	0.31×10^{-2}	3.34×10^{-2}
4	2.46×10^{-2}	1.76×10^{-2}	0	0.92×10^{-2}	0.22×10^{-2}	3.08×10^{-2}
5	0	0	3.04×10^{-2}	0.345×10^{-2}	0.345×10^{-2}	2.35×10^{-2}
6	0	0	7.58×10^{-2}	0.86×10^{-2}	0.86×10^{-2}	5.86×10^{-2}

It is evident from experiments 1, 2, 3 and 4 that

Number of moles of dihydrogen reacted = number of moles of iodine reacted = $\frac{1}{2}$ (number of moles of HI formed).

Also, experiments 5 and 6 indicate that,

$$[H_{2(g)}]_{eq} = [I_{2(g)}]_{eq}$$

Knowing the above facts, in order to establish a relationship between concentrations of the reactants and products, several combinations can be tried. Let us consider the simple expression,

$$\frac{[HI_{(g)}]_{eq}}{[H_{2(g)}]_{eq}[I_{2(g)}]_{eq}}$$

It can be seen that if we put the equilibrium concentrations of the reactants and products, the above expression is far from constant. However, if we consider the expression,

$$\frac{[HI_{(g)}]^2_{eq}}{[H_{2(g)}]_{eq}[I_{2(g)}]_{eq}}$$

We find that this expression gives constant value in all the six cases as below:

Experiment Number	$[HI_{(g)}]_{eq}/[H_{2(g)}]_{eq}[I_{2(g)}]_{eq}$	$[HI_{(g)}]^2_{eq}/[H_{2(g)}]_{eq}[I_{2(g)}]_{eq}$
1	1840	46.4
2	1610	47.6
3	1400	46.7
4	1520	46.9
5	1970	46.4
6	790	46.4

It can be seen that in this expression the power of the concentration for reactants and products are actually the stoichiometric coefficients in the equation for the chemical reaction. Thus, for the reaction

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

the equilibrium constant K_c is written as,

$$K_c = \frac{[HI_{(g)}]^2_{eq}}{[H_{2(g)}]_{eq}[I_{2(g)}]_{eq}}$$

Generally, the subscript 'eq' (used for equilibrium) is omitted from the concentration terms. It is taken for granted that the concentrations in the expression for K_c are equilibrium values. We, therefore, write,

$$K_c = \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]}$$

The subscript 'C' indicates that K_c is expressed in concentrations of mol L⁻¹.

At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

Important

➥ *Equilibrium constant is always defined when equilibrium is achieved. At equilibrium reaction does not stop, it occurs in the backward and forward directions at equal rates.*

The equilibrium constant for a general reaction,

$$aA + bB \rightleftharpoons cC + dD$$

is expressed as,

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

where [A], [B], [C], and [D], are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,

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

is written as

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

Molar concentration of different species is indicated by enclosing these in the square bracket and, as mentioned above, it is implied that these are equilibrium concentrations. While writing an expression for the equilibrium constant, a symbol for phases (s, l, g) are generally ignored.

Characteristics of Equilibrium Constant

(1) Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

Let us write equilibrium constant for the reaction,

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

as,

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

The equilibrium constant for the reverse reaction,

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

at the same temperature is,

$$K'_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{x} = \frac{1}{K_c}$$

Thus, $K'_c = \dfrac{1}{K_c}$

(2) If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor(n) then we must make sure that the expression for equilibrium constant also reflects that change i.e., value of equilibrium constant becomes $(K_c)^n$. For example, if the reaction is written as,

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$$

The equilibrium constant for the above reaction is given by:

$$K''_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}}$$

$$= \left\{\frac{[HI]^2}{[H_2][I_2]}\right\}^{\frac{1}{2}} = K_c^{\frac{1}{2}}$$

On multiplying the equation by n,

we get,

$$nH_{2(g)} + nI_{2(g)} \rightleftharpoons 2nHI_{(g)}$$

Therefore, equilibrium constant for the reaction is equal to K_c^n. It should be noted that because the equilibrium constants K_c and K'_c have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of equilibrium constant.

(3) The equilibrium constant does not depend upon initial concentration and has a definite value for every chemical reaction at a given temperature.

(4) If any chemical reaction is completed in more than one step, then equilibrium constant for overall reaction is equal to the product of the equilibrium constant of all steps.

(5) The pure solids and liquids are not considered for calculation K_c because they have constant concentration if one of the reactants or products is gas.

Example 1.2: Cased Based:

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reactions occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium. A mixture of reactants and products is found at equilibrium.

(A) Under a given set of experimental conditions, with an increase in the concentration of the reactants, the rate of a chemical reaction:

- **(a) Decreases**
- **(b) Increases**
- **(c) Remains unaltered**
- **(d) First decreases and then increases**

(B) Which of the following statement is correct?

- **(a) An irreversible reaction goes to almost completion.**
- **(b) A reversible reaction always goes to completion if carried out in a closed vessel.**
- **(c) At equilibrium, the rate of forward reaction becomes equal to that of the backward reaction.**
- **(d) In the beginning, the rate of backward reaction is much greater than that of the forward reaction.**

(C) What will be the forward and backward reactions rate of a chemical reaction at chemical equilibrium?

(D) Show how the reaction rates and concentrations change with respect to time in the following reaction.

$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)}$$

(E) Assertion (A): In dynamic equilibrium, forward and backward reactions continue to take place at equal rates.

Reason (R): In dynamic equilibrium, colour and density change with time.

- **(a) Both (A) and (R) are true and (R) is the correct explanation of (A).**
- **(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).**
- **(c) (A) is true but (R) is false.**
- **(d) (A) is false but (R) is true.**

Ans. (A) *(b) Increases*

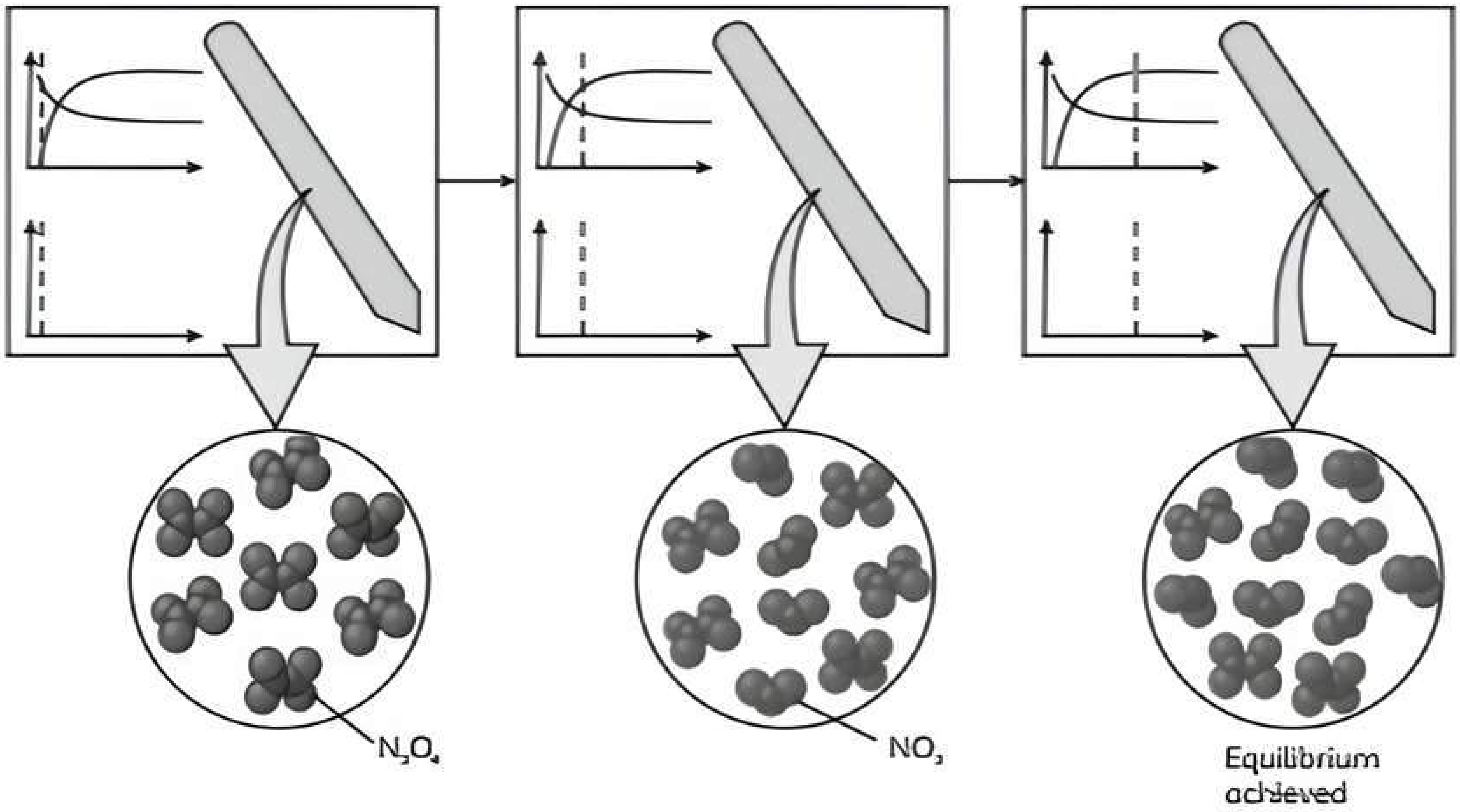
Explanation: Increasing the concentration of one or more reactants will often increase the rate of reaction. This occurs because a higher concentration of a reactant will lead to more collisions of that reactant in a specific time period.

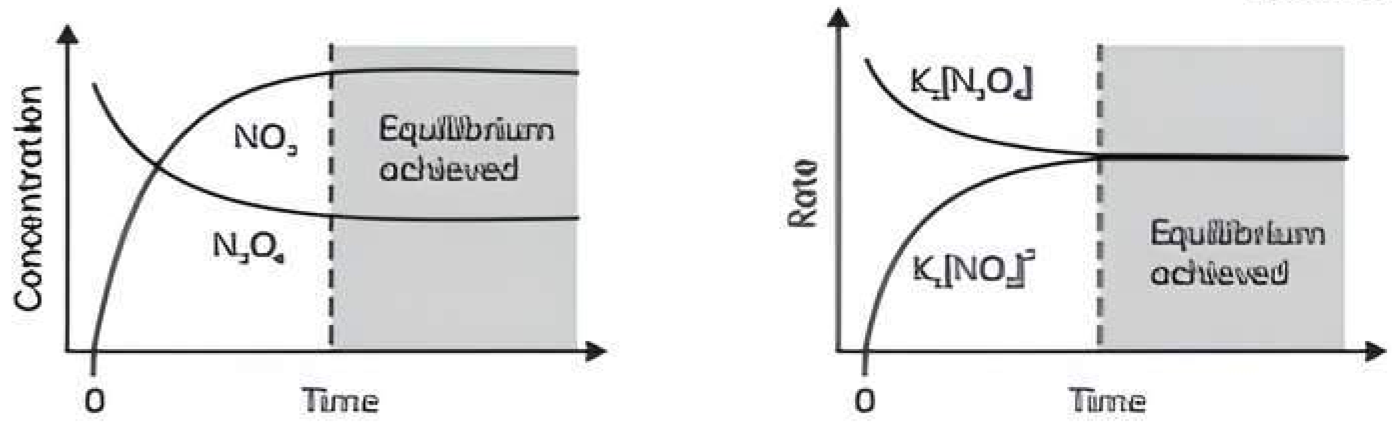
(B) *(c) At equilibrium, the rate of forward reaction becomes equal to that of backward reaction.*

Explanation: Chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. A forward reaction is a reaction in which products are produced from reactants and it goes from left to right in a reversible reaction. A backward reaction is a reaction in which reactants are produced from products and it goes from right to left in a reversible reaction. Chemical equilibrium is achieved when the rate of the forward reaction is equal to the rate of the backward reaction.

(C) In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products.

(D) The concentration of reactant starts decreasing with time and that of the product increases with time till equilibrium is reached and from equilibrium, there is no change in concentration of reactant and product.





(E) *(c) (A) is true but (R) is false.*

Explanation: Chemical equilibrium is the state in which the forward reaction rate and the reverse reaction rate are equal, so assertion is true but there is no change in density at equilibrium, so reason is false.

Example 1.3: The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500 K. $[N_2] = 1.5 \times 10^{-2}$ M, $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2 \times 10^{-2}$ M. Calculate equilibrium constant. [NCERT]

Ans. The equilibrium constant for the reaction

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

Can be written as,

$$K_c = \frac{\left[NH_{3(g)}\right]^2}{\left[N_{2(g)}\right]\left[H_{2(g)}\right]^3}$$

$$= \frac{\left(1.2\times10^{-2}\right)^2}{\left(1.5\times10^{-2}\right)\left(3.0\times10^{-2}\right)^3}$$

$$= 355.55$$

or $$= 3.55 \times 10^2$$

Example 1.4: At equilibrium, the concentrations of $N_2 = 3.0 \times 10^{-3}$ M, $O_2 = 4.2 \times 10^{-3}$ M and $NO = 2.8 \times 10^{-3}$ M in a sealed vessel at 800 K. What will be K_c for the reaction?

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

Ans. For the reaction equilibrium constant, K_c can be written as,

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

$$= \frac{\left(2.8\times10^{-3}M\right)^2}{\left(3.0\times10^{-3}M\right)\left(4.2\times10^{-3}M\right)}$$

$$= 0.622$$

Example 1.5: Write the expression for the equilibrium constant, K_c for each of the following reactions:

(A) $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

(B) $2Cu(NO_3)_{2(s)} \rightleftharpoons 2CuO_{(s)} + 4NO_{2(g)} + O_{2(g)}$

(C) $CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$

(D) $Fe^{3+}_{(aq)} + 3OH^{-}_{(aq)} \rightleftharpoons Fe(OH)_{3(s)}$

(E) $I_{2(s)} + 5F_{2(g)} \rightleftharpoons 2IF_{5(g)}$ [NCERT]

Ans. The expressions for the equilibrium constants are:

(A) $$K_c = \frac{\left[NO_{(g)}\right]^2\left[Cl_{2(g)}\right]}{\left[NOCl_{(g)}\right]^2}$$

(B) $$K_c = \frac{\left[CuO_{(s)}\right]^2\left[NO_{2(g)}\right]^4\left[O_{2(g)}\right]}{\left[Cu(NO_3)_{2(s)}\right]^2}$$

Concentration in solid states is taken as unity.

Hence, $[CuO] = 1[Cu(NO_3)_{2(s)}] = 1$

$K_c = [NO_{2(g)}]^4 [O_{2(g)}]$

(C) $$K_c = \frac{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}][H_2O_{(l)}]}$$

$$= \frac{[CH_3COOH_{(aq)}][C_2H_5OH_{(aq)}]}{[CH_3COOC_2H_{5(aq)}]}$$

(D) $$K_c = \frac{[Fe(OH)_{3(s)}]}{[Fe^{3+}_{(aq)}][OH^-_{(aq)}]^3}$$

$$= \frac{1}{[Fe^{3+}_{(aq)}][OH^-_{(aq)}]^3}$$

(E) $$K_c = \frac{[IF_5]^2}{[I_{2(s)}][F_2]^5} = \frac{[IF_5]^2}{[F_2]^5}$$

TOPIC 4

HOMOGENEOUS EQUILIBRIA

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

For example, in the gaseous reaction,

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

Reactants and products are in the homogeneous phase. Similarly, for the reactions,

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

and, $Fe^{3+}_{(aq)} + SCN^-_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$

All the reactants and products are in a homogeneous solution phase. Now consider the equilibrium constant for some homogeneous reactions.

Equilibrium Constant in Gaseous Systems

We have expressed the equilibrium constant of the reactions in terms of the molar concentration of the reactants and products, and used the symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressure.

The ideal gas equation is written as,

$$PV = nRT$$

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

Here, P is the pressure in Pa, n is the number of moles of the gas, V is the volume in m^3 and T is the temperature in Kelvin. Therefore, $\frac{n}{V}$ is concentration expressed in mol/m^3.

If concentration C, is in mol/L or mol / dm^3, and P is in bar then,

$$P = CRT$$

We can also write $P = [\text{gas}]\, RT$

Here, $R = 0.0831$ bar litre/mol K

At constant temperature, the pressure of the gas is proportional to its concentration, i.e. $P \propto [\text{gas}]$

For reaction in equilibrium

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

We can write either

$$K_c = \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]}$$

$$K_c = K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})}$$

Further, since

$$P_{HI} = [HI_{(g)}]\,RT$$
$$P_{I_2} = [I_{2(g)}]\,RT$$
$$P_{H_2} = [H_{2(g)}]\,RT$$

Therefore,

$$K_p = \frac{(P_{HI})^2}{(P_{H_2})(P_{I_2})} = \frac{[HI_{(g)}]^2[RT]^2}{[H_{2(g)}]RT\,[I_{2(g)}]RT}$$

$$= \frac{[HI_{(g)}]^2}{[H_{2(g)}][I_{2(g)}]} = K_c$$

In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case.

For example, in reaction

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

$$K_p = \frac{(P_{NH_3})^2}{(P_{N_2})(P_{H_2})^3}$$

$$= \frac{[NH_{3(g)}]^2[RT]^2}{[N_{2(g)}]RT\,[H_{2(g)}]^3(RT)^3}$$

$$= \frac{[NH_{3(g)}]^2[RT]^{-2}}{[N_{2(g)}][H_{2(g)}]^3} = K_c(RT)^{-2}$$

Or $K_p = K_c (RT)^{-2}$

Similarly, for a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

$$K_p = \frac{(P_C^c)(P_D^d)}{(P_A^a)(P_B^b)} = \frac{[C]^c[D]^d(RT)^{(c+d)}}{[A]^a[B]^b(RT)^{(a+b)}}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{(c+d)-(a+b)}$$

$$= \frac{[C]^c[D]^d}{[A]^a[B]^b}(RT)^{\Delta n} = K_c (RT)^{\Delta n_g}$$

Where $\Delta n_{(g)}$ = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation. It is necessary that while calculating the value of K_p, pressure should be expressed in bar as the standard state for pressure is 1 bar.

1 Pascal (Pa) = 1 Nm^{-2} and 1 bar = 10^5 Pa

Example 1.6: PCl_5, PCl_3, and Cl_2 are at equilibrium at 500 K and have a concentration of 1.59M PCl_3, 1.59M Cl_2 and 1.41M PCl_5.

Calculate K_c for the reaction,

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ [NCERT]

Ans. The equilibrium constant K_c for the above reaction can be written as,

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$= \frac{(1.59)^2}{(1.41)}$$

$$= 1.79$$

Example 1.7: The value of K_c = 4.24 at 800 K for the reaction

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

Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K, if only CO and H_2O are present initially at a concentration of 0.10 M each.

Ans. For the reaction,

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

Initial concentration	0.1M	0.1M	0	0

Let x mole of each of the products being formed.

At equilibrium:

(0.1 – x) M (0.1 – x) M x M xM

Where x is the amount of CO_2 and H_2 at equilibrium.

Hence, equilibrium constant can be written as,

$$K_c = \frac{x^2}{(0.1-x)^2} = 4.24 = 4.24$$

$x^2 = 4.24\,(0.01 + x^2 - 0.2x)$

$x^2 = 0.0424 + 4.24\,x^2 - 0.848x$

$3.24\,x^2 - 0.848\,x + 0.0424 = 0$

$a = 3.24,\ b = -0.848,\ c = 0.0424$

(for quadratic equation $ax^2 + bx + c = 0$,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{0.848 \pm \sqrt{(0.848)^2 - 4 \times 3.24 \times 0.0424}}{2 \times 3.24}$$

$$x = \frac{0.848 \pm \sqrt{0.719104 - 0.549504}}{6.48}$$

$$x = \frac{0.848 \pm 0.4118}{6.48}$$

$$x_1 = \frac{0.848 - 0.4118}{6.48} = 0.067$$

$$x_2 = \frac{0.848 + 0.4118}{6.48} = 0.194$$

The value x_2 should be neglected because it will give a concentration of the reactant which is more than the initial concentration.

Hence, the equilibrium concentrations are,

$[CO_2] = [H_2] = x = 0.067$ M

$[CO] = [H_2O] = 0.1 - 0.067 = 0.033$M

Example 1.8: For the equilibrium,

$2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$ the value of the equilibrium constant is 3.75×10^{-4} at 1069 K. Calculate the K_p for the reaction at this temperature.

Ans. We know that,

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

For the above reaction,

$$\Delta n_{(g)} = (2 + 1) - 2 = 1$$

$$K_p = 3.75 \times 10^{-4}\,(8.314 \times 1069)$$

$$K_p = 3.33$$

Related Theory

- *When reactants and products are given in the gas phase, equilibrium constant is defined in the terms of partial pressure.*

TOPIC 5

HETEROGENEOUS EQUILIBRIA

Equilibrium in a system having more than one phase is called heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium.

$$H_2(O)_{(l)} \rightleftharpoons H_2O_{(g)}$$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution is a heterogeneous equilibrium.

$$Ca(OH)_{2(s)} + H_2O \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$$

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (*i.e.*, independent of the amount present). In other words, if a substance X is involved, then $[X_{(s)}]$ and $[X_{(l)}]$ are constant, whatever the amount of 'X' is taken. Contrary to this, $[X_{(g)}]$ and $[X_{(aq)}]$ will vary as the amount of X in a given volume varies. Let us take the thermal dissociation of calcium carbonate which is an interesting and important example of heterogeneous chemical equilibrium.

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

On the basis of the stoichiometric equation, we can write,

$$K_c = \frac{\left[CaO_{(s)}\right]\left[CO_{2(g)}\right]}{\left[CaCO_{3(s)}\right]}$$

Since $[CaCO_{3(s)}]$ and $[CaO_{(s)}]$ are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K_c = [CO_{2(g)}]$$

$$K_p = P_{CO_2}$$

This shows that at a particular temperature, there is a constant concentration or pressure of CO_2 in equilibrium with $CaO_{(s)}$ and $CaCO_{3(s)}$. Experimentally, it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $CaCO_{3(s)}$ and $CaO_{(s)}$ is 2.0×10^5 Pa. Therefore, equilibrium constant at 1100 K for the above reaction is:

$$K_p = P_{CO_2} = 2 \times 10^5\ Pa / 10^5\ Pa = 2.00$$

Similarly, in the equilibrium between nickel, carbon monoxide and nickel carbonyl (used in the purification of nickel),

$$Ni_{(s)} + 4CO_{(g)} \rightleftharpoons Ni(CO)_{4(g)}$$

the equilibrium constant is written as

$$K_c = \frac{\left[Ni(CO)_4\right]}{\left[CO\right]^4}$$

It must be remembered that in heterogeneous equilibrium pure solids or liquids must be present (however small they may be) for the equilibrium to exist, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction,

$$Ag_2O_{(s)} + 2HNO_{3(aq)} \rightleftharpoons 2AgNO_{3(aq)} + H_2O_{(l)}$$

$$K_c = \frac{\left[AgNO_3\right]^2}{\left[HNO_3\right]^2}$$

Units of equilibrium constant: Equilibrium constant is the ratio of the concentrations raised to the stoichiometric coefficients.

Therefore, the unit of the equilibrium constant $= [\text{Mole L}^{-1}]^{\Delta n}$ or $[\text{atm}]^{\Delta n}$

If the number of gaseous moles of reactants and products is the same, then K_p and K_c both are unitless.

Example 1.9: The value of K_p for the reaction, $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$ is 3.0 at 1000 K. If initially $P_{CO_2} = 0.48$ bar and $P_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2.

Ans. For the reaction, let 'x' be the amount of CO_2 reacted, then

	$CO_{2(g)} + C_{(s)} \rightleftharpoons$	$2CO_{(g)}$
Initial pressure:	0.48 bar	0
At equilibrium:	(0.48–x)bar	$2x$ bar

$$K_p = \frac{P^2_{CO}}{P_{CO_2}}$$

$$K_p = \frac{(2x)^2}{(0.48 - x)} = 3$$

$$4x^2 = 3\,(0.48 - x)$$

$$4x^2 = 1.44 - 3x$$

$$4x^2 + 3x - 1.44 = 0$$

$$a = 4,\ b = 3,\ c = -1.44$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-3 \pm \sqrt{(3)^2 - 4 \times 4 \times (-1.44)}}{2 \times 4}$$

$$x = \frac{-3 \pm \sqrt{9 + 23.04}}{8}$$

(As value of x cannot be negative. Hence, we neglect that value)

$$x = \frac{-3 \pm 5.66}{8} = 0.33$$

The equilibrium partial pressures are,

$P_{CO} = 2x = 2 \times 0.33 = 0.66$ bar

$P_{CO_2} = 0.48 - x = 0.48 - 0.33 = 0.15$ bar

OBJECTIVE Type Questions

[1 mark]

Multiple Choice Questions

1. Equilibrium constant K_p for the following reaction.

$$MgCO_{3(s)} \rightleftharpoons MgO_{(s)} + CO_{2(g)}$$

(a) $K_p = P_{CO_2}$

(b) $K_p = P_{CO_2} \times \frac{P_{CO_2} \times P_{MgO}}{P_{MgCO_3}}$

(c) $K_p = \frac{P_{CO_2} \times P_{MgO}}{P_{MgCO_3}}$

(d) $K_p = \frac{P_{MgCO_3}}{P_{CO_2} \times P_{MgO}}$

Ans. *(a)* $K_p = P_{CO_2}$

Explanation: All the terms of the solid phase are removed in equilibrium constant equation.

$$K_p = \frac{P_{MgO} \times P_{CO_2}}{P_{MgCO_3}} = P_{CO_2}$$

2. We know that the relationship between K_c and K_p is $K_p = K_c (RT)^{\Delta n}$. What would be the value of $\Delta n_{(g)}$ for the reaction:

$NH_4Cl_{(s)} \rightarrow NH_{3(g)} + HCl_{(g)}$

(a) 1 (b) 0.5

(c) 1.5 (d) 2 [NCERT Exemplar]

Ans. *(d) 2*

Explanation: We know that $K_p = K_c (RT)^{\Delta n_{(g)}}$

For the reaction $\Delta n_{(g)} = (1 + 1) - 0 = 2$

3. At 500 K, the equilibrium constant K_c for the following reaction is 5.

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)}$$

What would be the equilibrium constant K_c for the reaction?

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

(a) 0.04 (b) 0.4

(c) 25 (d) 2.5

[NCERT Exemplar]

Ans. *(a) 0.04*

Explanation: If the reaction is reversed, the value of the equilibrium constant is reciprocated and if the reaction is multiplied by a factor (*n*) then the value of the equilibrium constant becomes $K'_c = (K_c)^n$

$$K'_c = (K_c)^2$$

$$= (5)^2 = 25$$

$$K'_c = \frac{1}{25} = 0.04$$

4. For the hypothetical reactions, the equilibrium constant (*K*) values are given

$A \rightleftharpoons B : K_1 = 2$

$B \rightleftharpoons C : K_2 = 4$

$C \rightleftharpoons D : K_3 = 8$

The equilibrium constant (*K*) for the reaction $A \rightleftharpoons D$ is

(a) 48 (b) 24

(c) 12 (d) 64

[Delhi Gov. QB 2022]

Ans. *(d) 64*

Explanation: To get the desired reaction, we need to add all three equations.

When reactions are added, equilibrium constants are multiplied.

So, $K = K_1 \times K_2 \times K_3 = 2 \times 4 \times 8 = 64$.

5. **In which of the following reaction $K_p > K_c$?**

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

(b) $H_{2(g)} + I_2(g) \rightleftharpoons 2HI_{(g)}$

(c) $PCl_{3(g)} + Cl_2(g) \rightleftharpoons PCl_{5(g)}$

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

Ans. *(d)* $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

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

Where $\Delta n_{(g)}$ = (Number of moles of gaseous products) – (Number of moles of gaseous reactants) Thus,

(a) $\Delta n = 2 - (3 + 1) = 2 - 4 = -2$

(b) $\Delta n = 2 - (1 + 1) = 2 - 2 = 0$

(c) $\Delta n = 1 - (1 + 1) = 1 - 2 = -1$

(d) $\Delta n = (2 + 1) - 2 = 1$

6. **Partial pressure of O_2 in the given reaction is**

$$2\,Ag_2O_{(s)} \rightleftharpoons 4\,Ag_{(s)} + O_{2(g)}$$

(a) K_p (b) $\sqrt{K_p}$

(c) $\sqrt[3]{K_p}$ (d) $2\,K_p$

Ans. *(a)* K_p

Explanation: Both solid phase substances have partial pressure equal to unity.

$$K_p = \frac{\left[P_{Ag(s)}\right]^4 \left[P_{O_{2(g)}}\right]}{\left[P_{Ag_2O(s)}\right]^2} = \left[P_{O_2}\right]$$

7. **What is the unit of equilibrium constant for the given reaction?**

$$BaCO_{3(s)} \rightleftharpoons BaO_{(s)} + CO_{2(g)}$$

(a) bar (b) $molL^{-1}$

(c) Litre (d) mol^2L^{-2}

Ans. *(b) mol L^{-1}*

Explanation: The pure solids and liquids are not considered for the calculation of K_c because they have constant concentration. if one of the reactants or products is gas then the value of equilibrium constant is determined only through gaseous molecule. Thus, in this case, the units of equilibrium constant are only dependent on CO_2 molecule.

8. If the equilibrium constant of stepwise reaction is

$$N_2 + O_2 \rightleftharpoons 2\,NO,\ K_1$$
$$2NO + O_2 \rightleftharpoons 2NO_2\ K_2$$

Then, the value of the equilibrium constant for the reaction $N_2 + 2O_2 \rightleftharpoons 2NO_2$ is:

(a) $K_1 + K_2$
(b) $\frac{K_1}{K_2}$
(c) $K_1 - K_2$
(d) $K_1 \times K_2$

Ans. *(d) $K_1 \times K_2$*

Explanation: If any chemical reaction is completed in more than one step, then equilibrium constant for overall reaction is equal to the product of equilibrium constant of all steps.

Assertion-Reason (A-R)

In the following question no. (9-11) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

9. Assertion (A): Increasing the concentration of H_2 will increase the magnitude of equilibrium constant of the reaction.

$$H_2 + I_2 \rightleftharpoons 2HI$$

Reason (R): Value of K_c depends upon the concentration of reactants and products taken.

Ans. *(d) (A) is false but (R) is true.*

Explanation: The value of equilibrium constant does not depend upon the initial concentration of reactant.

Related Theory

According to Le Chatelier's principle, factors like concentration, pressure, temperature and inert gases that affect equilibrium are changed and the equilibrium will shift in that direction where the effects caused by these changes are nullified.

10. Assertion (A): For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R): Equilibrium constant is independent of temperature.

[NCERT Exemplar]

Ans. *(c) (A) is true but (R) is false.*

Explanation: The equilibrium constant has a definite value for every chemical reaction at a given temperature.

11. Assertion (A): Chemical equilibrium represents a state of a reversible reaction in which properties of the system (pressure, concentration, etc.) become constant under the given set of conditions.

Reason (R): The chemical equilibrium is a state of rest in which opposite reactions stop.

Ans. *(c) (A) is true but (R) is false.*

Explanation: At equilibrium, all the macroscopic properties such as pressure and concentration become constant but at equilibrium, both forward and backward reaction work in opposite direction.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

12. *When we increase the pressure on a system in which NO, O_2 and NO_2 are at equilibrium:*

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

The formation of additional amounts of NO_2 decreases the total number of molecules in the system because each time two molecules of NO_2 form, a total of three molecules of NO and O_2 are consumed. This reduces the total pressure exerted by the system but does not completely relieve, the stress of the increased pressure. On the other hand, a decrease in the pressure on the system favours decomposition of NO_2 into NO and O_2 which tends to restore the pressure.

Now consider this reaction:

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

Because there is no change in the total number of molecules in the system during the reaction, a change in pressure does not favour either formation or decomposition of gaseous nitrogen monoxide.

(A) Which type of equilibrium is established for the following: Ice ⇌ Water?

(B) What is the effect of pressure on the equilibrium constant?

(C) What will happen to the concentrations of N_2, O_2 and NO at equilibrium if a catalyst is added?

Ans. (A) It is a heterogeneous equilibrium because all reactants and products are in the different phase. When pressure is applied to the equilibrium state, $V_{Ice} > V_{Water}$. Thus, an increase in pressure will show a forward reaction.

(B) Equilibrium constant is not changed if you change the pressure of the system. The only thing that changes an equilibrium constant is a change of temperature. The position of equilibrium may be changed if you change the pressure.

(C) When a catalyst is added it basically has no effect on the equilibrium of the reaction. A catalyst only increases the speed of reaction or more so the forward and reverse reaction rates are equal. When this happens, the system will reach equilibrium faster.

13. *Let us consider a system at equilibrium consisting of a number of phases-vapour, solid and liquid-of various components. We shall assume that it is shut off from outside action by a rigid non-conducting envelope. This means no loss of generality, as, if the system is already in equilibrium, it will still be so if enclosed in such an envelope. The following results are obtained:*

***(1) Thermal Conditions:** The temperature must be uniform; otherwise, heat will flow from high to low temperature.*

***(2) Mechanical Conditions:** If only ordinary hydrostatic pressure is considered it, must be everywhere equal, but if gravity is taken into account of or membranes are present this must be modified.*

***(3) Chemical Conditions:** The variable which determines chemical equilibrium is not so familiar as temperature, pressure or electrical potential and a few words are there for necessary in explanation of what is best called the "chemical potential" of a substance. Consider a particular substance present in two different phases and for a moment deal with these phases separately. Let a supply of the substance be available in a reference state and an infinitesimal amount of it pass from this state to one of the phases. Keep the volume and entropy of the phase constant by subtracting heat and changing the pressure.*

(A) What do you mean by phase equilibrium?

(a) No reaction

(b) Study of equilibrium which exists between or within different states of matter namely solid, liquid and gas.

(c) All reactants must be in the same phase.

(d) Product concentration is more.

(B) Which property of the phases must be equal when phases of a system are in thermodynamic equilibrium with each other?

(a) Chemical potential

(b) Volume

(c) Temperature

(d) Pressure

(C) When does equilibrium exist between the phases of a substance?

(a) At 0 K

(b) At 1073 K

(c) At the triple point

(d) At 273 K

(D) Can four phases exist in equilibrium?

(a) Yes **(b) No**

(c) Can't define **(d) In certain case**

(E) When solid and liquid phases are in equilibrium?

(a) Melting point **(b) Freezing point**

(c) Never **(d) Both (a) and (b)**

Ans. (A) *(b) Study of equilibrium which exists between or within different states of matter namely solid, liquid and gas.*

Explanation: Phase equilibrium is the study of the equilibrium which exists between or within different states of matter namely solid, liquid and gas.

(B) *(a) Chemical potential*

Explanation: The chemical potential of the component of a thermodynamic system in a given phase is a thermodynamic state function.

(C) *(c) At the triple point*

Explanation: In thermodynamics, the triple point of a substance is the temperature and pressure at which the three phases of that substance coexist in thermodynamic equilibrium.

(D) *(a)* Yes

Explanation: Four phases of a substance composed of a single component can coexist at thermal equilibrium.

(E) *(d)* both *(a)*

Explanation: The melting point of a solid is the same as the freezing point of the liquid. At that temperature, the solid and liquid states of the substance are in equilibrium. For water, this equilibrium occurs at 0°C.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

14. **Write the unit of K_c and K_p for the reaction $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$**

Ans. $K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(mol\,L^{-1})^2}{(mol\,L^{-1})} = mol\,L^{-1}$

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}} = \frac{bar^2}{bar} = bar$$

15. **How does K affected by endothermic reaction if temperature is increased?**

[Delhi Gov. QB 2022]

Ans. Endothermic reactions are the reactions which absorb heat – an increase in temperature will shift the equilibrium in the endothermic direction (left). This will favour the formation of reactants and a decrease in K_{eq}.

16. **At 500 K, equilibrium constant, K_c, for the following reaction is 5.**

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)} \qquad \text{—(i)}$$

What would be the equilibrium constant K_c for the reaction?

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

Ans. On reversing and then multiplying the equation (i) we get the desired equation. Thus, equilibrium constant for desired equation would be

$$K_c^{\prime} = \frac{1}{K_c^2} = \frac{1}{(5)^2} = \frac{1}{25} = 0.04$$

17. **Write the chemical equation for the following chemical constant.**

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

Ans. The chemical equation is given by the following reaction:

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

18. **K_p and K'_p are the equilibrium constants of the two reactions, $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$ and $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ respectively. What is the relation between the two constants?**

Ans. When the balanced chemical reaction has an equilibrium constant, K_p is multiplied by a certain value and the equilibrium constant for the new equation will be $(K_p)^n$.

In the given reaction, $n = 2$.

So, $K'_p = (K_p)^2$

$\Rightarrow$ $K_p = \sqrt{K'_p}$

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

19. **In the chemical equilibrium the rate constant of a backward reaction is 5×10^{-3} and the equilibrium constant is 2^{-5}, then what is the rate constant of the forward reaction?**

Ans. In chemical equilibrium the equilibrium constant,

$$K = \frac{\text{Rate constant for forward reaction, } K_f}{\text{Rate constant for backward reaction, } K_b}$$

So, $K_f = K \times K_b$

$$= 5 \times 10^{-3} \times 2^{-5}$$

$$= \frac{5 \times 10^{-3}}{32}$$

$$= 1.56 \times 10^{-3}$$

20. **PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1} respectively. Find the value of K_c for the reaciton.**

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

Ans.
$$K_c = \frac{[1.2\times10^{-3}][1.2\times10^{-3}]}{[0.8\times10^{-3}]}$$
$$= \frac{[1.44\times10^{-6}]}{[0.8\times10^{-3}]}$$
$$= 1.8 \times 10^{-3}$$

21. Find out the value of K_c of the following equilibria from the value of K_p:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$
$$K_p = 167 \text{ atm at } 1073\ K$$

Ans. $K_p = K_c\,(RT)^{\Delta n_{(g)}}$

$\Delta n_{(g)} = 1$

$$K_c = \frac{167}{[(0.0821)(1073)^1]} = 1.90$$

22. Bromine monochloride, BrCl, decomposes into bromine and chlorine and reaches the equilibrium $2BrCl_{(g)} \rightleftharpoons Br_{2(g)} + Cl_{2(g)}$ for which K_c = 32 at 500K. If initially pure BrCl is present at a concentration of 3.30×10^{-3} mol litre^{-1}; what is its molar concentration in the mixture at equilibrium?

Ans.

	$2BrCl_{(g)}$	$\rightleftharpoons Br_{2(g)}$	$+ Cl_{2(g)}$
Initial concentration	0.0033	0	0
Concentration at equilibrium	(0.0033−a)	$\frac{a}{2}$	$\frac{a}{2}$

$$K_c = \frac{[Br_2][Cl_2]}{[BrCl]^2} = 32$$

$$= \frac{\frac{a}{2}\times\frac{a}{2}}{[0.0033-a]^2} = 32$$

$$= \frac{a}{2\times(0.0033-a)} = 5.66$$

$$a = 3 \times 10^{-3}$$

$$[BrCl] = 3.3 \times 10^{-3} - 3 \times 10^{-3}$$
$$= 0.3 \times 10^{-3}$$
$$= 3 \times 10^{-4}$$

Caution

The stoichiometric coefficients of the reactants and products are always written as their power of the concentration in the equilibrium equation.

23. For the reversible reaction, $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 500°C, the value of K_p is 1.44×10^{-5} atm^{-2}. Find the K_c value.

[Delhi Gov. QB 2022]

Ans. The relationship between K_p and K_c is given by the equation

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

$\Delta n_{(g)}$ = Number of moles of gaseous products − number of moles of gaseous reactants $= 2 - 4 = -2$

$$K_p = K_c\,(RT)^{-2}$$

Given $K_p = 1.44 \times 10^{-5}$ atm^{-2}. T = 500°C = 500 + 273 = 773 K

$$1.44 \times 10^{-5} = K_c\,(0.082 \times 773)^{-2}$$

$$K_c = \frac{1.44\times10^{-5}}{(0.082\times773)^{-2}} = 0.0578$$

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

24. For the reaction: $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

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

Some reactions are written below in Column I and their equilibrium constants in terms of K_c are written in Column II. Match the following reactions with the corresponding equilibrium constant

Column I (Reaction)	Column II (Equilibrium Constant)
(A) $2N_{2(g)} + 6H_{2(g)} \rightarrow 4NH_{3(g)}$	(i) $2K_c$
(B) $2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$	(ii) $K_c^{\frac{1}{2}}$
(C) $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightarrow NH_{3(g)}$	(iii) $\frac{1}{K_c}$
	(iv) K_c^2

[NCERT Exemplar]

Ans. (A) (iv) K_c^2

Explanation: When the reaction is multiplied by a factor(n) then the value of equilibrium constant becomes $K'_c = (K_c)^n$.

(B) (iii) $\frac{1}{K_c}$

Explanation: When the reaction is reversed, the value of equilibrium constant is reciprocated.

(C) (ii) $K_c^{1/2}$

Explanation: When the reaction is multiplied by a factor $\left(\frac{1}{2}\right)$ then the value of equilibrium constant becomes $K'_c = (K_c)^{1/2}$.

25. A gas is in equilibrium with water at a certain temperature and pressure. What will happen if:

(A) Temperature is increased

(B) Pressure of gas is increased?

Ans. (A) Increasing the temperature always decreases the solubility of gases. The gas molecules in a liquid are dissolved by the process of dissolution. As we know that dissolution is an exothermic process, the solubility should decrease with an increase in temperature to validate Le Chatelier's principle.

(B) According to Le Chatelier's principle when we increase the pressure equilibrium shifts towards that side which has less number of moles. So in this case when pressure is increased equilibrium will shift towards that side which has fewer moles. Solubility of a gas in water will increase.

26. (A) Explain why pure liquids and solids can be ignored while writing the value of equilibrium constants.

(B) Elaborate with an example of

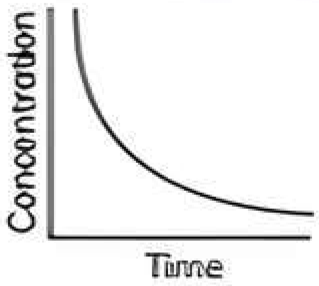
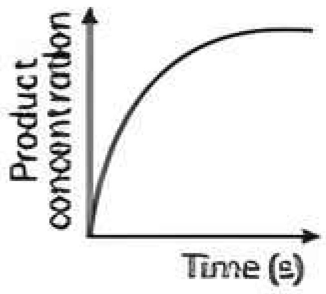
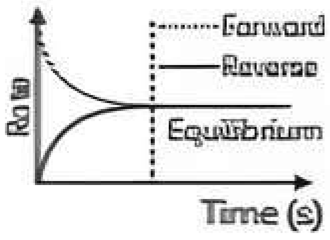
$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

Ans. (A) Pure solids and liquids are not included in the equilibrium constant expression because molar concentration of a fine solid or liquid is independent of the amount present. Since density of pure liquid or solid is fixed and molar mass is also fixed. Therefore, molar concentration is constant. They do not affect the reactant amount at equilibrium in the reaction, so they are disregarded and kept at 1.

(B) Value of equilibrium constant for this reaction is $K_p = \frac{(P_{H_2})^4}{(P_{H_2O})^4}$

In this, both solid phase compound is eliminated while writing equilibrium constant equation because molar concentration of a fine solid or liquid is independent of the amount present, i.e. it will remain constant.

27. Match the following graphical variation with their description.

Column I	Column II
(A) 	(i) Variation in product concentration with time
(B) 	(ii) Reaction at equilibrium
(C) 	(iii) Variation in reactant concentration with time

[NCERT Exemplar]

Ans. (A) *(iii)* Variation in reactant concentration with time

Explanation: Reactant concentrations decrease with time as reactants are converted to products.

(B) *(i)* Variation in product concentration with time

Explanation: Since products are formed with time so their concentration increases with time.

(C) *(ii)* Reaction at equilibrium

Explanation: At equilibrium after some time, the rate of the forward reaction is equal to the rate of the reverse reaction. No further changes occur in the concentrations of reactants and products, even though the two reactions continue at equal but opposite rates.

28. Following data is given for the reaction:

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

$\Delta_f H^\circ [CaO_{(s)}] = -635.1\ KJ\ mol^{-1}$

$\Delta_f H^\circ [CO_{2(g)}] = -393.5\ KJ\ mol^{-1}$

$\Delta_f H^\circ [CaCO_{3(s)}] = -1206.9\ KJ\ mol^{-1}$

Predict the effect of temperature on the equilibrium constant of the above reaction.

Ans. Enthalpy of a reaction can be calculated using the formula

$\Delta_r H$ = Sum of enthalpies of formation of the product – sum of the enthalpies of formation of the reactants.

Thus for the reaction,

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

Enthalpy of reaction can be calculated as:

$$\Delta_r H^\circ = \Delta_f H^\circ[CaO_{(s)}] + \Delta_f H^\circ[CO_{2(g)}] - \Delta_f H^\circ[CaCO_{3(s)}]$$

$$= (-635.1\ KJ\ mol^{-1}) + (-393.5\ KJ\ mol^{-1}) - (-1206.9\ KJ\ mol^{-1})$$

$$= 178.3\ kJ\ mol^{-1}$$

The reaction is endothermic. Hence, an increase in temperature will shift the equilibrium in the endothermic direction (left). This will favour the formation of reactants and a decrease in K_{eq}.

LONG ANSWER Type Questions (LA)

[**4** & **5** marks]

29. Explain the variation in equilibrium constant with change in:

(A) Concentration **(B) Pressure**

(C) Temperature **(D) Catalyst**

Ans. (A) Equilibrium constants are not changed if you change the concentrations of things present in the equilibrium. The position of equilibrium is changed if you change the concentration of something present in the mixture.

(B) Equilibrium constants are not changed if you change the pressure of the system. The position of equilibrium may be changed if you change the pressure. That means that if you increase the pressure, the position of equilibrium will move in such a way as to decrease the pressure again - if that is possible. It can do this by favouring the reaction which produces the fewer molecules. If there are the same number of molecules on each side of the equation, then a change of pressure makes no difference to the position of equilibrium.

(C) Equilibrium constants are changed if you change the temperature of the system. Increasing the temperature decreases the value of the equilibrium constant. Where the forward reaction is endothermic, increasing the temperature increases the value of the equilibrium constant. The position of equilibrium also changes if you change the temperature.

(D) Equilibrium constants are not changed if you add (or change) a catalyst. The position of equilibrium is not changed if you add a catalyst. A catalyst speeds up both the forward and backward reactions by exactly the same amount. Dynamic equilibrium is established when the rates of the forward and backward reactions become equal. If a catalyst speeds up both reactions to the same extent, then they will remain equal without any need for a shift in the position of equilibrium.

30. (A) What do you understand by reversible and irreversible reaction? Give two examples of each.

(B) What do you understand by the term reaction at equilibrium? Is it a static equilibrium?

(C) Show that the reaction at equilibrium can be characterised by an equilibrium constant, defined as

$$K = \frac{K_f}{K_b}$$

Where K_f and K_b are the rate constants for the forward and backward reaction?

Ans. (A) **Reversible Reactions:** In reversible reactions, the reactants and products are never fully consumed; they are each constantly reacting and being produced. A reversible reaction can take the following summarised form:

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

This reversible reaction can be broken into two reactions.

Reaction 1: $A + B \xrightarrow{k_f} C + D$

Reaction 2: $C + D \xrightarrow{k_b} A + B$

These two reactions are occurring simultaneously, which means that the reactants are reacting to yield the products, as the products are reacting to produce the reactants. Collisions of the reacting molecules cause chemical reactions in a closed system. After products are formed, the bonds between these products are broken when the molecules collide with each other, producing sufficient energy needed to break the bonds between the product and reactant molecules.

Examples: Reaction of hydrogen gas and iodine vapour to form hydrogen iodide.

Nitrogen reacts with hydrogen to produce ammonia.

Irreversible Reactions: A fundamental concept of chemistry is that chemical reactions occurred when reactants reacted with each other to form products. These unidirectional reactions are known as irreversible reactions, reactions in which the reactants convert to products and where the products cannot convert back to the reactants.

Examples: These reactions are essentially like baking. The ingredients, acting as the reactants, are mixed and baked together to form a cake, which acts as the product. This cake cannot be converted back to the reactants (the eggs, flour, etc.), just as the products in an irreversible reaction cannot convert back into the reactants.

An example of an irreversible reaction is combustion. Combustion involves burning an organic compound—such as a hydrocarbon—and oxygen to produce carbon dioxide and water. Because water and carbon dioxide are stable, they do not react with each other to form the reactants. Combustion reactions take the following form:

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

(B) When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. Eventually, this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its *equilibrium state*, or more simply, "at equilibrium".

Related Theory

- *The equilibrium composition is independent of the direction from which it is approached (i.e., the initial conditions).*
- *Reactions at dynamic equilibrium are reversible (can proceed in either direction), those at static equilibrium are irreversible and can only proceed in one direction.*

(C) Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the decomposition reaction of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$\text{forward rate} = K_f[N_2O_4]$$

and reverse rate $= K_b[NO_2]^2$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

so

$$\frac{K_f}{K_b} = \frac{[NO_2]^2}{[N_2O_4]}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{K_f}{K_b}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

31. Write equilibrium constant for the following reaction:

(A) $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$

(B) $KClO_{3(s)} \rightleftharpoons KCl_{(s)} + \frac{3}{2}O_{2(g)}$

(C) $CaC_{2(s)} + 5O_{2(g)} \rightleftharpoons 2CaCO_{3(s)} + 2CO_{2(g)}$

(D) $Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}_{(aq)}$

(E) $CuSO_4 \cdot 5H_2O_{(s)} \rightleftharpoons CuSO_{4(s)} + 5H_2O_{(vapour)}$

Ans. (A) $K_c = \frac{[NO_2]^2}{[N_2O_4]}$

(B) $K_p = [O_2]^{3/2}$

(C) $K_p = \frac{[P_{CO_2}]^2}{[P_{O_2}]^5}$

(D) $K_c = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]}$

(E) $K_p = [P_{H_2O}]^5$

Caution

- *Equilibrium expressions for the heterogeneous equilibria involving a pure solid or a pure liquid can be simplified by removing their concentrations or partial pressure from the equation because the molar concentration of a pure solid or liquid remains constant (i.e., independent of the amount present).*

APPLICATIONS OF EQUILIBRIUM 2

TOPIC 1

APPLICATIONS OF EQUILIBRIUM CONSTANT

Before giving the applications of the equilibrium constant let's have a look at some of the important features of the equilibrium constants:

Important Features of the Equilibrium Constant

(1) When concentrations of the reactants and products have attained a constant value at equilibrium state, then only expression for the equilibrium constant is applicable.

(2) The value of the equilibrium constant is independent of the initial and final concentrations of the reactants and products.

(3) At a given temperature, the equilibrium constant has one unique value for each reaction represented by a balanced equation. Equilibrium constant is temperature dependant.

(4) The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.

(5) The equilibrium constant for a reaction is related to the equilibrium constant of the equivalent reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

Applications of the Equilibrium Constant

(1) To predict the extent of the reaction on the basis of its magnitude

(2) To predict the direction of the reaction

(3) To calculate the equilibrium concentrations.

Predicting the extent of the reaction

The extent of magnitude of a reaction is determined by the numerical value of its equilibrium constant. But the equilibrium constant does not provide any information about the rate at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products and inversely proportional to the concentrations of the reactants.

Some overviews about the composition of equilibrium mixtures are as follows:

If $K_c > 10^3$, product predominates over reactants and the reaction proceeds nearly to completion.

Example:

$$H_{2(g)} + Cl_{2(g)} \rightleftharpoons 2HCl_{(g)} \text{ at 300 K has } K_c = 4.0 \times 10^{31}$$

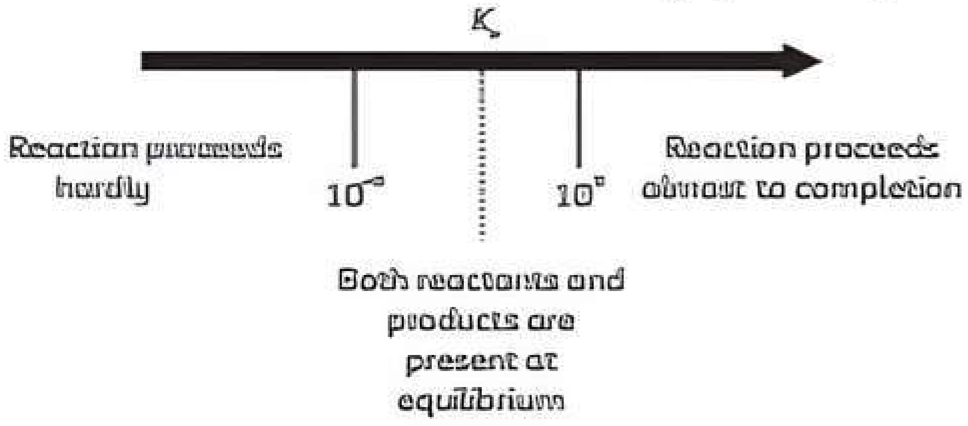
$$H_{2(g)} + Br_{2(g)} \rightleftharpoons 2HBr_{(g)} \text{ at 300 K has } K_c = 5.4 \times 10^{18}$$

If $K_c < 10^{-3}$, the reactants predominate over the product and the reaction proceeds rarely.

The decomposition of H_2O into H_2 and O_2 at 500K has a very small equilibrium constant, $K_c = 4.1 \times 10^{-48}$.

If K_c is in range of 10^{-3} to 10^3, considerable concentration for both reactants and products is present.

The gas phase decomposition of N_2O_4 to NO_2 have $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.



Predicting the extent of reaction based on K_c

Predicting the direction of the reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. We have to calculate the reaction quotient for this purpose. For a general reaction:

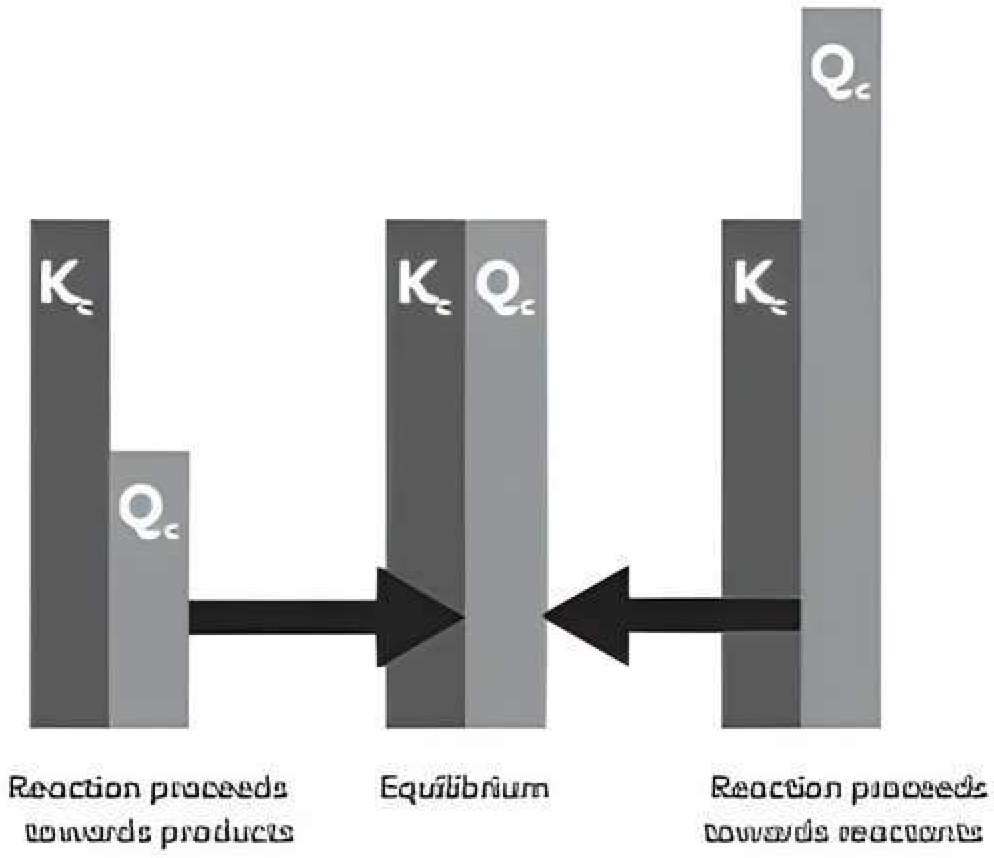
$$aA + bB \rightleftharpoons cC + dD$$

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

(1) If $Q_c > K_c$ the reaction will proceed in the reverse direction.

(2) If $Q_c < K_c$ the reaction will proceed in the forward direction.

(3) If $Q_c = K_c$, the reaction mixture is already at equilibrium.



Example 2.1: The equilibrium constant, K_c for the reaction: $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_3$ at 500 K is 0.061.

At a specific time, from the analysis, we can conclude that the composition of the reaction mixture 3.0 mol L^{-1} of N_2, 2.0 mol L^{-1} H_2 and 0.5 mol L^{-1} of NH_3. Find out whether the reaction is at equilibrium or not. If not, find in which direction the reaction proceeds to reach equilibrium.

[NCERT]

Ans. $N_{2(g)} \quad + \quad 3H_{2(g)} \quad \rightleftharpoons \quad 2NH_3$

3.0 mol L^{-1} 2.0mol L^{-1} 0.5 mol L^{-1}

$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3}$$
$$= 0.0104$$

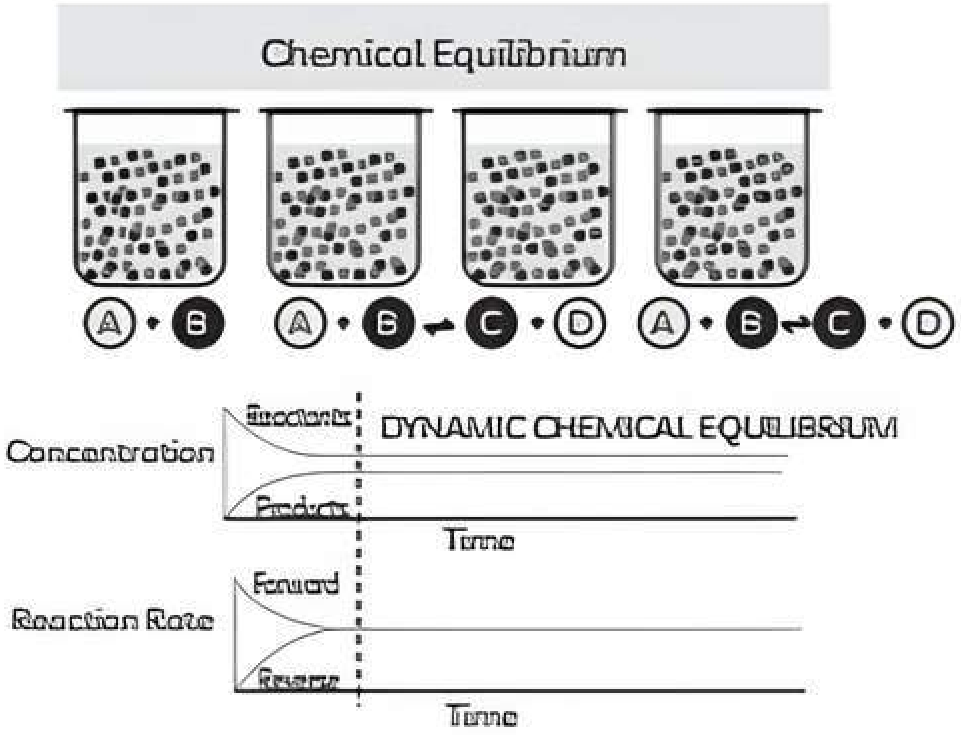
Given that $K_c = 0.061$

$\therefore Q_c \neq K_c$ the reaction is not at equilibrium.

$\therefore Q_c < K_c$ the reaction proceeds in the forward direction to reach the equilibrium.

Example 2.2: Case Based:

Equilibrium reactions and non-equilibrium reactions are the two types of chemical reactions that can occur in a system. When the reactants are not entirely dissociated into their ions, the reaction becomes an equilibrium reaction. The full ionisation of reactants is a non-equilibrium reaction. The words reaction quotient and equilibrium constant are used to describe the chemical processes that take place in a system. The reaction quotient indicates how many chemical species are present in a reaction mixture. The ratio between the concentrations of products and reactants is known as the equilibrium constant. The fundamental distinction between response quotient and equilibrium constant is that the former may be computed at any time while the latter can only be calculated at the point of equilibrium.



(A) When H_2 is mixed with I_2 and equilibrium is attained, then:

- (a) Amount of HI formed is equal to the amount of I_2 dissociated
- (b) The reaction stops completely
- (c) Dissociation of HI stop
- (d) None of the above

(B) Which of the following factors favours the reverse reaction in the chemical equilibrium?

- (a) Increasing the concentration of reactants
- (b) Increasing the concentration of one or more products
- (c) Increasing the pressure
- (d) Removal of at least one of the products at regular interval

(C) For the reaction $PCl_3 + Cl_2 \rightleftharpoons PCl_5$ the value of $K_c = 25$, then what is the value of K_p at a temperature of 250°C?

(D) The dissociation constant for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. What will be the equilibrium constant for the equilibrium reaction $CH_3COOH + CN^- \rightleftharpoons HCN + CH_3COO^-$?

(E) Assertion (A): The value of equilibrium constant K, gives us a relative idea about the extent to which a reaction proceeds.

Reason (R): The value of K is independent of the stoichiometry of reactants and products at the point of equilibrium.

- (a) Both (A) and (R) are true and (R) is the correct explanation of (A).
- (b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
- (c) (A) is true but (R) is false.
- (d) (A) is false but (R) is true.

Ans. (A) *(b) The reaction stops completely*

Explanation: When H_2 is mixed with I_2 and equilibrium is attained, then the reaction stops completely because at equilibrium the rate of the forward reaction is equal to the rate of backward reaction.

(B) *(b) Increasing the concentration of one or more products.*

Explanation: An increase in the concentration of one of the products shifts the equilibrium in the reverse direction i.e., in the favour of the formation of the product.

(C) *According to the given reaction:*

$PCl_3 + Cl_2 \rightleftharpoons PCl_5$

$$K_p = K_c (RT)^{\Delta n_{(g)}}$$
$$\Delta n_{(g)} = 1 - 2 = -1$$
$$K_p = 25 \times (0.082 \times 523)^{-1}$$
$$K_p = 0.58$$

(D) The equilibrium constant for individual reactions:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_1 = 1.5 \times 10^{-5} = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_2 = 4.5 \times 10^{-10} = \frac{[CN^-][H^+]}{[HCN]}$$

Now, $CH_3COOH + CN^- \rightleftharpoons HCN + CH_3COO^-$

$$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]} = \frac{K_1}{K_2}$$
$$= \frac{1}{4.5 \times 10^{-10}} \times 1.5 \times 10^{-5} = 3.33 \times 10^4$$

(E) *(c) (A) is true but (R) is false.*

Explanation: The value of equilibrium constant, K gives us a relative idea about the extent to which a reaction proceeds either in forward, backward or remains in equilibrium.

The value of K is dependent on the stoichiometry of reactants and products at the point of equilibrium. For example, if the reaction is multiplied by 2, the equilibrium constant is squared.

So, the assertion is true and the reason is false.

Calculating the equilibrium concentrations

If we know the initial concentration but don't know the equilibrium concentrations then the following steps shall be followed:

Step 1: Write the balanced equation for the given reaction.

Step 2: Make the table that lists for each substance involved in the reaction:

(a) The initial concentration

(b) The change in the concentration on reaching the equilibrium

(c) The equilibrium concentration

In the table, define x as the concentration (mol/L) of one of the chemicals that reacts when the reaction reaches equilibrium, then use the stoichiometry of the reaction to calculate the concentrations of the other substances in terms of x.

Step 3: Solve the value of x after substituting the equilibrium concentration into an equilibrium equation for the reaction.

Step 4: Calculate the equilibrium concentrations from the calculated value of x.

Step 5: Check the results by substituting them into the equilibrium equation.

Example 2.3: 13.8 g of N_2O_4 was placed in a 1 L reaction vessel at 400 K and allowed to attain equilibrium $N_2O_{4(g)} \rightleftarrows 2NO_{2(g)}$. The total pressure at equilibrium was found to be 9.15 bar. Calculate K_c, K_p and partial pressure at equilibrium. [NCERT]

Ans. We know that $PV = nRT$

Total volume (V) = 1L

The molecular mass of N_2O_4 = 92 g

Number of moles 13.8/92g = 0.15 of the gas (n)

Gas constant (R) = 0.083 bar L mol^{-1}K^{-1}

Temperature = 400 K

From equation: $PV = nRT$

$P \times 1L = 0.15 mol \times 0.083$ bar L mol^{-1}K$^{-1} \times 400$ K

P = 4.98 bar

$N_2O_4 \rightleftharpoons 2NO_2$

Initial pressure : 4.98

	N_2O_4	$\rightleftharpoons 2NO_2$
Initial pressure	4.98	0
At	$4.98 - x$	$2x$

Hence, $P_{[illegible]}$ at equilibrium $= P_{N_2O_4} + P_{NO_2}$

$$= 4.98 - x + 2x$$
$$9.15 = (4.98 - x) + 2x$$
$$9.15 = 4.98 + x$$
$$x = 9.15 - 4.98$$
$$x = 4.17 \text{ bar}$$

Partial pressure at equilibrium is:

$$P_{N_2O_4} = 4.98 - 4.17 = 0.81 \text{bar}$$
$$P_{NO_2} = 2x = 2 \times 4.17 = 8.34 \text{ bar}$$

$$K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}}$$
$$= \frac{(8.34)^2}{0.81} = 85.87$$
$$K_p = K_c(RT)^{\Delta n_{(g)}}$$
$$85.87 = K_c(0.083 \times 400)^1$$
$$K_c = 2.586 = 2.6$$

TOPIC 2

RELATION BETWEEN EQUILIBRIUM CONSTANT (K_c), REACTION QUOTIENT (Q_c) AND GIBBS ENERGY (G)

The value of K_c for the reaction does not depend on the rate of reaction. It is related to the thermodynamics of the reaction and change in Gibbs energy, ΔG.

If:

(1) ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.

(2) ΔG is positive, then the reaction is non-spontaneous and goes in the backward direction.

(3) ΔG is zero, then the reaction has achieved equilibrium. No free energy is left to drive the reaction at this point.

Free energy change (ΔG) is related to the standard Gibbs free energy (ΔG°) as follows:

$$\Delta G = \Delta G^\circ + RT \ln Q_c$$

Or $$\Delta G = \Delta G^\circ + 2.303RT \log Q_c$$

At equilibrium the $\Delta G = 0$ and $Q_c = K_c$

∴ $$\Delta G^\circ = -RT \ln K_c$$

or $$\Delta G^\circ = -2.303RT \log K_c$$

Taking antilog on both sides:

$$K = e^{-\Delta G^\circ/RT}$$

Important

- *The reaction spontaneity can be interpreted as:*

(1) If K>1 then ΔG = -ve, i.e., reaction is spontaneous and proceeds in the forward direction.

(2) If K<1 then ΔG = +ve, i.e., reaction is non-spontaneous and proceeds in the forward direction to such a small extent that only a minute quantity of product is formed. Hence the reaction is spontaneous in the backward direction.

Example 2.4: **The value of ΔG° for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. Find the value of K_c at 298 K. [NCERT]**

Ans. Given: ΔG° = 13.8 kJ/mol = 13.8 × 10³ J/mol

$$\Delta G^\circ = -RT \ln K_c$$

$$= \frac{-13.8 \times 10^3\ \text{J/mol}}{8.314\ \text{J/mol}^{-1}\text{K}^{-1} \times 298\ \text{K}}$$

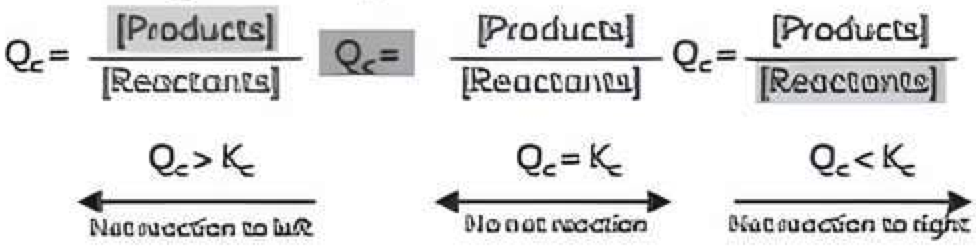
Hence, $$\ln K_c = -5.569$$

$$K_c = e^{-5.569}$$

$$K_c = 3.81 \times 10^{-3}$$

Example 2.5: Case Based:

Equilibrium is the process in which properties like pressure, temperature and volume show no change. The equilibrium constant is used to characterise the equilibrium condition. This equilibrium constant is the ratio of the concentration of product to reactant raised by the power of stoichiometric quotient. This same ratio at conditions other than equilibrium is known as reaction quotient and their difference is represented if the reaction proceeds in a forward or backward direction. The relation is developed between the reaction quotient Q_c, equilibrium constant K_c and Gibbs energy. Josiah Willard Gibbs invented Gibb's energy in the 1870s. He originally referred to this energy as a system's "available energy." "Graphical Methods in the Thermodynamics of Fluids," was the paper he released in 1873 which explained how his equation could anticipate the behaviour of systems when they were coupled.



(A) The value of K_c for the reaction $2X \rightleftharpoons Y + Z$ is 2.0×10^{-3}. At the given time the composition of the reaction mixture is $[X] = [Y] = [Z] = 3 \times 10^{-4}$ M. In which direction will the reaction proceed?

(a) Forward

(b) Backward

(c) Equilibrium is attained

(d) None of the above

(B) When is the reaction non-spontaneous?

(a) Gibbs free energy is positive.

(b) Gibbs free energy is negative.

(c) Does not depend on Gibbs free energy.

(d) Gibbs free energy is zero.

(C) The extent of dissociation of PCl_5 at a certain temperature is 20% at one atm pressure. Calculate the pressure at which the substance is 50% dissociated at the same temperature.

(D) The Gibbs energy change for the reaction ΔG° = 63.3 kJ. Calculate the K_c of $Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+_{(aq)} + CO_3^{2-}{}_{(aq)}$ at room temperature.

(E) Assertion (A): Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.

Reason (R): Equilibrium constant depends upon the way in which the reaction is written.

(a) **Both (A) and (R) are true and (R) is the correct explanation of (A).**

(b) **Both (A) and (R) are true but (R) is not the correct explanation of (A).**

(c) **(A) is true but (R) is false.**

(d) **(A) is false but (R) is true.**

Ans. **(A)** *(b) Backward*

Explanation: According to the given reaction: $2X \rightleftharpoons Y + Z$ the value of Q_c is calculated as:

$$Q_c = \frac{[Y][Z]}{[X]^2} = \frac{3\times10^{-4}\times3\times10^{-4}}{3\times10^{-4}\times3\times10^{-4}} = 1$$

Therefore, $Q_c > K_c$ so, the reaction will go in the backward direction.

(B) *(a) Gibbs free energy is positive.*

Explanation: The Gibbs free energy is non-spontaneous when its value is positive. A very small amount of product is formed or we can say that it favours the backward reaction.

(C) The dissociation reaction can be given as:

	PCl_5	$\rightleftharpoons$	PCl_3	$+ Cl_2$
P at 1 atm	1–0.2		0.2	0.2
P at *x* atm	1–0.5		0.5	0.5

$$K_p = \frac{(0.2/1.2)(0.2/1.2)}{(0.8/1.2)} \text{ at 1 atm}$$

$$= \frac{(0.5\times x/1.5)(0.5\times x/1.5)}{(0.5\times x/1.5)}$$

$$x = \frac{1.5\times0.04}{1.2\times0.8\times0.5} = 0.125$$

(D) Standard Gibbs energy is denoted as:

$\Delta G^\circ = -2.303RT \log K_c$

$63.3 \times 10^3 J = -2.303 \times 8.314 \times 298 \log K_c$

$\log K_c = -11.09$

$K_c = 10^{-11.09}$

$K_c = 8 \times 10^{-12}$

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: $H_2 + I_2 \rightleftharpoons 2HI$

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

For the reverse reaction:

$$2HI \rightleftharpoons H_2 + I_2$$

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{K_c}$$

TOPIC 3

FACTORS AFFECTING EQUILIBRIA

A system attains equilibrium under a specific set of conditions and remains in the same state of equilibrium as long as these conditions are maintained constant. A change in these conditions disturbs the equilibrium and causes a net reaction to occur. This reaction helps the system to attain equilibrium again although the new state of equilibrium is different from the earlier one. Before discussing about these factors, we should first learn about Le-Chatelier's principle that will help in qualitative prediction about the effect of a change in conditions on equilibrium.

Le-Chatelier's Principle

In order to predict the effect of changing the conditions of the system at equilibrium, Henry Louis Le Chatelier, a French chemist, proposed a general principle in 1884. The principle is commonly known as Le Chatelier's principle. The principle can be stated as follows:

When a constraint (stress) is applied on a system at equilibrium, the system behaves in such a way so as to undo the effect of the constraint.

The principle can also be stated as follows:

If a system at equilibrium is subjected to a change which displaces it from the equilibrium, a net reaction will occur in a direction that opposes the change.

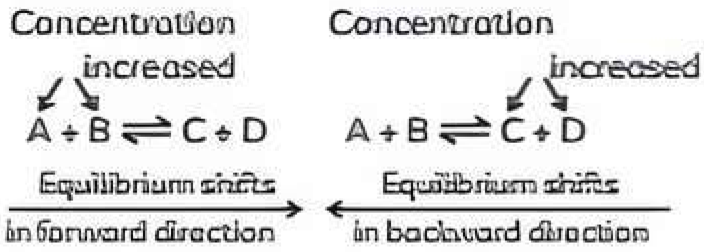
Le Chatelier's principle can be applied to any physical or chemical system at equilibrium. To a chemical system at equilibrium, the constraint can be applied by changing the concentration of reactants or products, by changing the pressure of the system, or by changing the temperature. Therefore, for a chemical system at equilibrium, Le Chatelier's principle can also be stated as given below.

"When a chemical system at equilibrium is subjected to a change in concentration, pressure, or temperature; the equilibrium shifts in the direction that undo the change."

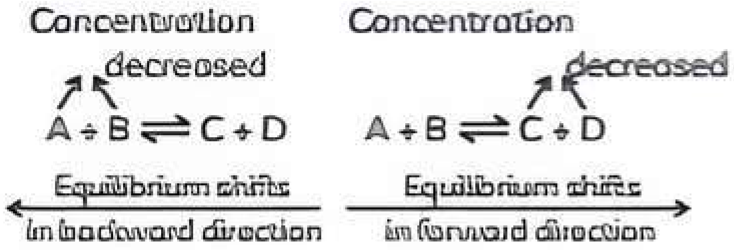
Le Chatelier's principle is very helpful in the qualitative prediction of the effect of a change in concentration, pressure, or temperature. Now we shall discuss about the factors affecting chemical equilibrium.

Effect of concentration change

According to Le Chatelier's principle, a system at equilibrium has a tendency to counteract any change imposed on it. Therefore, when the concentration of a substance is changed, the equilibrium shifts in the direction in which the effect of the change of concentration could be reduced. For example, if the concentration of a particular reactant is increased, the system would like to reduce the amount of the added substance. This is possible only when the reactants combine to form the products. Thus, forward reaction occurs and the equilibrium shifts towards right. In case the concentration of a product is increased, the equilibrium shifts towards left in order to decrease the amount of the added substance. Thus, for a general reaction A+B → C+D, we have



Similarly, a decrease in concentration of any of the reactants will cause the equilibrium to shift towards left (backward reaction will occur) while a decrease in the concentration of any of the products will cause the equilibrium to shift towards right (i.e. forward reaction will occur).



Hence, for the present specific case of the change in concentration, Le Chatelier's principle can be restated as follows.

When the concentration of any of the reactants or products is changed, the system readjusts itself by shifting the equilibrium in a direction which counteracts the change in concentration that was made.

Let us consider some specific examples to see the effect of a change in concentration.

(1) Formation of complex ferric thiocyanide ion: The formation of this ion can be represented as

$$\underset{\text{(yellow)}}{Fe^{3+}_{(aq)}} + \underset{\text{(colourless)}}{SCN^-_{(aq)}} \rightleftharpoons \underset{\text{(deep red)}}{[Fe(SCN)]^{2+}_{(aq)}}$$

In this reaction Fe^{3+} and $FeSCN^{2+}$ ions are coloured and possess yellow and deep red colours respectively whereas SCN^- ions are colourless. When a salt capable of giving Fe^{3+} ions (e.g. $FeCl_3$) or a salt capable of giving SCN^- ions (e.g. $FeSCN^{2+}$) is added, the colour of the reaction mixture becomes deep red. This indicates that the equilibrium has shifted towards right and the forward reaction involving the combination of Fe^{3+} and SCN^- ions to give $FeSCN^{2+}$ ions occurred. This is in accordance with Le Chatelier's principle. If a small amount of sodium fluoride is added, the colour of the solution becomes lighter. This is because F^- ions are given by sodium fluoride combined with Fe^{3+} ions and decrease their concentration. Removal of Fe^{3+} ions causes the equilibrium to shift towards left i.e., deep red-coloured $FeSCN^{2+}$ ions dissociate to give yellow-coloured Fe^{3+} ions. Thus, the colour becomes lighter.

(2) Formation of lime in a lime kiln: In a lime kiln, the lime (CaO) is prepared by the decomposition of limestone ($CaCO_3$) according to the following equation.

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

Lime cannot be formed effectively until the equilibrium shifts in the forward direction. This can be achieved by the continuous removal of $CO_{2(g)}$. The design of lime kiln is such that the carbon dioxide formed in the reaction escapes continuously. According to Le Chatelier's principle, removal of CO_2 gas (i.e. decrease in the concentration of CO_2) causes the equilibrium to shift towards right to compensate for the loss of CO_2 escaped. Thus, a forward reaction occurs and the limestone continuously decomposes to give lime.

(3) Formation of ammonia: The reaction involving the formation of ammonia is as follows.

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

At equilibrium, the concentration of ammonia becomes constant and no more ammonia is formed. Therefore to effect the formation of more ammonia, the equilibrium must be made to shift in the forward direction. According to Le Chatelier's principle, this can be achieved either by increasing the concentration of N_2 (or H_2) or by decreasing the concentration of ammonia. In Haber's process (the process used for the manufacture of ammonia), the ammonia formed is continuously removed from the reaction site by liquefaction. This compels the system to form more and more ammonia in the quest of attaining equilibrium.

(4) Transport of oxygen by haemoglobin to the tissues: The red corpuscles present in our blood contain haemoglobin (Hb). It carries oxygen that we inhale to the tissues of the body. Haemoglobin combines with oxygen in the lungs to form oxyhaemoglobin (HbO_2) according to the equation

$$Hb_{(s)} + O_{2(g)} \rightleftharpoons HbO_{2(s)}$$

In the tissues the partial pressure of oxygen is low. Therefore in tissues, in accordance with Le Chatelier's principle, the above equilibrium shifts towards left to increase the partial pressure of oxygen. Thus, oxyhaemoglobin decomposes to give up the oxygen to the tissues.

(5) Removal of CO_2 from the tissues by the blood: In addition to supplying oxygen to tissues, blood removes CO_2 from them. The equilibrium involved is

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO^-_{3(aq)}$$

The partial pressure of CO_2 in tissues is high. Therefore, CO_2 dissolves in water present in the blood. In lungs, partial pressure of CO_2 is low.

Therefore, when the blood returns to the lungs, the above equilibrium shifts towards left and CO_2 dissolved in blood gets released from it.

Effect of pressure change

The effect of change in pressure is significant only for those systems which involve gaseous substances and the equilibrium reaction involves a net increase or decrease in the number of moles (i.e. $\Delta n \neq 0$) of the gaseous substances. For this specific case, Le Chatelier's principle can be restated as follows.

When pressure is increased (or decreased) on a system containing gaseous substances in equilibrium, then the equilibrium shifts in that direction which tends to decrease (or increase) the pressure and hence to decrease (or increase) the number of moles.

The pressure of a gaseous system is proportional to the total number of moles of substances present in it. If a reaction involves the decrease in the number of moles, the pressure of the system will decrease. Similarly, a reaction involving an increase in the number of moles tends to increase the pressure of the system. Let us consider the following general reaction.

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

$$Q_c = \frac{\left[C_{(g)}\right]^c \left[D_{(g)}\right]^d}{\left[A_{(g)}\right]^a \left[B_{(g)}\right]^b}$$

With an increase in pressure, the volume of the system (products) decreased and hence, the value of Q_c decreases (i.e. $Q_c << K_c$). Thus, in order to achieve the equilibrium again, the reaction proceeds in the forward direction.

For example, let us consider the following reaction.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}; \Delta H = -22.4\,\text{kcal}$$

$$Q_c = \frac{\left[NH_{3(g)}\right]^2}{\left[N_{2(g)}\right]\left[H_{2(g)}\right]^3}$$

This reaction proceeds with a decrease in number of moles in the forward direction. More ammonia can be formed only when the pressure on the system is increased. An increase in the pressure decreases the volume and hence an increases in the number of moles present in the unit volume. According to Le Chatelier's principle, the equilibrium must shift in the forward direction to oppose the increase in a number of moles per unit volume. Hence more nitrogen and hydrogen combine to form more ammonia.

Example 2.6: **Does the number of moles of reaction products increase, decrease or remain the same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?**

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

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

(C) $3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$ **[NCERT]**

Ans. According to Le Chatelier's principle, on decreasing pressure equilibrium shifts in that direction where pressure increases (i.e. number of moles in gaseous state are more). Therefore, number of moles of products in

(A) increases

(B) decreases

(C) remains same. (If $\Delta n_g = 0$, there is no effect of change of pressure).

Example 2.7: Case Based:

Sometimes we can change the position of equilibrium by changing the pressure of a system. However, changes in pressure have a measurable effect only in systems in which gases are involved, and then only when the chemical reaction produces a change in the total number of gas molecules in the system. An easy way to recognize such a system is to look for different numbers of moles of gas on the reactant and product sides of the equilibrium. While evaluating pressure (as well as related factors like volume), it is important to remember that equilibrium constants are defined with regard to concentration (for K_c) or partial pressure (for K_p). Some changes to total pressure, like adding an inert gas that is not part of the equilibrium, will change the total pressure but not the partial pressures of the gases in the equilibrium constant expression. Thus, addition of a gas not involved in the equilibrium will not perturb the equilibrium. As we increase the pressure of a gaseous system at equilibrium, either by decreasing the volume of the system or by adding more of one of the components of the equilibrium mixture, we introduce a stress by increasing the partial pressures of one or more of the components. In accordance with Le Chatelier's principle, a shift in the equilibrium that reduces the total number of molecules per unit of volume will be favoured because this relieves the stress. The reverse reaction would be favoured by a decrease in pressure.

(A) Which of the following reactions will not get affected on increasing pressure?

(a) $2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$

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

(c) $CH_{4(g)} + 2S_{2(g)} \rightleftharpoons CS_{2(g)} + 2H_2S_{(g)}$

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

(B) In which of the following reactions the increase in pressure will favour the increase in products?

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

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

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

(d) $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

(C) A gas is in equilibrium with water at a certain temperature and pressure. What will happen if the pressure of the gas is increased?

(D) The dissociation of phosgene ($COCl_2$) is represented as follows:

$$COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$$

When a mixture of these three gases at equilibrium is compressed at a constant temperature, what happens to the partial pressure of $COCl_2$?

(E) Assertion (A): More ammonia can be formed only when the pressure on the system is increased.

Reason (R): An increase in the pressure decreases the volume and hence an increase in the number of moles present in the unit volume.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. (A) *(c)* $CH_{4(g)} + 2S_{2(g)} \rightleftharpoons CS_{2(g)} + 2H_2S_{(g)}$

Explanation: Since the number of moles of gaseous reactants and products are the same, the reaction will not be affected by changing the pressure.

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

Explanation: According to Le Chatelier's principle, the equilibrium must shift in forward direction to oppose the increase in number of moles per unit volume. Hence decrease in number of moles in the reaction makes it favourable at high pressure.

(C) If the pressure of the gas is increased the solubility of the gas in water will also increase.

(D) The partial pressure of $COCl_2$ increases when the mixture of these three gases at equilibrium is compressed at a constant temperature.

(E) *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: According to Le Chatelier's principle, the equilibrium must shift in forward direction to oppose the increase in number of moles per unit volume. Hence, more nitrogen and hydrogen combine to form more ammonia.

Effect of inert gas addition

Since inert gas does not take part in the reaction, so the equilibrium remains unaffected if the volume is kept constant. This is because at a constant volume, the partial pressures or the molar concentration of the substance involved in the reaction remain unchanged.

If an inert gas is added to an equilibrium process at constant pressure, the volume of the process will increase. Hence, the equilibrium will shift in a direction in which there is an increase in number of moles of the gases.

Effect of temperature change

At equilibrium, both forward and backward reactions occur simultaneously and in opposite directions. If one of the reactions is exothermic, the other must be endothermic, i.e. if the forward reaction proceeds with an evolution of heat, the backward reaction must involve absorption of heat. When the temperature is increased, the heat is added to the system. Therefore, according to Le Chatelier's principle, the equilibrium must shift in the direction which involves absorption of heat. Hence for the present case, Le Chatelier's principle can be stated as follows.

"When the temperature of a system at equilibrium is increased, the equilibrium shifts in that direction in which heat is absorbed."

For an exothermic reaction: In an exothermic reaction, the increase in temperature causes the backward reaction to occur resulting in an increase in the concentration of reactants. On the other hand, if the temperature of the system is decreased, heat is withdrawn. This compels the equilibrium to shift in the forward direction to compensate the loss of heat resulting in an increase in the concentration of products. Thus, in an exothermic reaction, a greater yield of products can be obtained by lowering the temperature.

$$\underset{\text{(Brown)}}{2NO_{2(g)}} \rightleftharpoons \underset{\text{(Colourless)}}{N_2O_{4(g)}} ;\Delta H = -57.2\ kJ\,mol^{-1}$$

When the temperature of this system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium should shift in the direction which involves the absorption of the added heat. Obviously, the backward reaction is endothermic. Therefore, the equilibrium shifts from right to left i.e., brown colour intensifies due to the formation of NO_2. On the other hand, decrease in temperature shifts the equilibrium towards right and more N_2O_4 is formed thereby decreasing the intensity of brown colour. Hence formation of N_2O_4 is possible only at low temperatures.

For an endothermic reaction: An increase in temperature in an endothermic reaction will help more reactants to combine together and to change in the products resulting in a higher yield of products. On the other hand, a decrease in temperature will favour the backward reaction to occur resulting in an increase in the concentration of reactants.

$$\underset{\text{pink}}{\left[Co(H_2O)_6\right]^{2+}_{(aq)}} + \underset{\text{colourless}}{4Cl^-_{(aq)}} \rightleftharpoons \underset{\text{blue}}{\left[CoCl_4\right]^{2-}_{(aq)}} + 6H_2O_{(l)}$$

The reaction is endothermic in the forward direction and exothermic in the backward direction. According to Le Chatelier's principle, an increase in temperature will favour the forward reaction to occur. Therefore, at room temperature, the colour of equilibrium mixture is blue due to $[CoCl_4]^{2-}$ while when cooled the mixture turns pink due to $[Co(H_2O)_6]^{2+}$.

Example 2.8: Case Based:

When hydrogen reacts with gaseous iodine, heat is evolved.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \Delta H = -9.4 \text{ kJ (exothermic)}$$

Because this reaction is exothermic, we can write it with heat as a product.

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

Increasing the temperature of the reaction increases the internal energy of the system. Thus, increasing the temperature has the effect of increasing the amount of one of the products of this reaction. The reaction shifts to the left to relieve the stress, and there is an increase in the concentration of H_2 and I_2 and a reduction in the concentration of HI. Lowering the temperature of this system reduces the amount of energy present, favours the production of heat, and favours the formation of hydrogen iodide. When we change the temperature of a system at equilibrium, the equilibrium constant for the reaction changes. Lowering the temperature in the HI system increases the equilibrium constant. At the new equilibrium the concentration of HI has increased and the concentrations of H_2 and I_2 decreased. Raising the temperature decreases the value of the equilibrium constant, from 67.5 at 357°C to 50.0 at 400°C.

(A) When I_2 dissociates to its atomic form the following reaction occurs:

$$I_{2(g)} \rightleftharpoons 2I_{(g)}; \Delta H = +150 \text{ kJ}$$

The reaction is favoured at:

(a) Low temperature
(b) High temperature
(c) No change in temperature
(d) High pressure

(B) The equilibrium constant of a reversible reaction at a given temperature:

(a) Depends on the initial concentration of reactants.
(b) Depends on the concentration of products at equilibrium.
(c) Does not depend on the initial concentration.
(d) It is not a characteristic of the reaction.

(C) A gas is in equilibrium with water at a certain temperature and pressure. What will happen if the temperature of the gas is increased?

(D) In which direction equilibrium is expected to shift on increasing temperature in the following reaction?

$$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}; \Delta H = +212 \text{ kcal}$$

(E) Assertion (A): For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R): Equilibrium constant is independent of temperature.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and R are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

Ans. **(A)** *(b) High temperature*

Explanation: Endothermic reaction is favoured at high temperature.

(B) *(c) Does not depend on initial concentration*

Explanation: Equilibrium constant is unaffected by changes in the concentrations of reactant and product.

(C) If the temperature is increased the solubility of the gas in water will decrease.

(D) $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}; \Delta H = +212 \text{ kcal}$

In the given reaction the equilibrium is expected to shift in forward direction on increasing temperature.

(E) *(c) (A) is true but (R) is false.*

Explanation: Equilibrium constant is temperature dependent.

Effect of Catalyst

A catalyst does not affect the state of equilibrium and the value of equilibrium constant remains the same no matter whether the catalyst is used or not. This is because a catalyst catalyses both forward and backward reactions to the same extent. Therefore, the values of K_1 and K_2 (rate constants for forward and backward reactions) increase to the same extent.

Hence, the value of equilibrium constant $\left(K = \frac{K_1}{K_2}\right)$ remains the same. Thus, the presence of a catalyst does not change the equilibrium point, it simply helps to attain the equilibrium faster.

Let us consider

- Haber's process of synthesis of ammonia

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}; \Delta H = -22.4 \text{ kcal}$$

Although low temperature favours the formation of NH_3, yet an optimum temperature is set, as the rate of reaction is very slow at low temperature. A temperature of 500°C is selected and a pressure of 200 atm is applied. To enhance the rate of reaction, a catalyst, finely divided iron containing molybdenum (acts as a promoter) is used.

Manufacture of sulphuric acid by contact process

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}; K_c = 1.7 \times 10^{26}$$

First step of the process is very slow so its speed is increased by using a catalyst like platinum or divanadium pentaoxide V_2O_5.

⚠ Caution

➥ *Usually, students get confused that catalyst is added as a reactant to be part of the reaction but the catalyst increases the rate of forward and backward reactions by the same factor hence, does not change the equilibrium constant.*

OBJECTIVE Type Questions

[**1** mark]

Multiple Choice Questions

1. **For the reaction $H_{2(g)} + I_{2(g)} \rightarrow 2HI$ the standard free energy is $\Delta G^\circ > 0$.**

   The equilibrium constant (K) would be___ .

   (a) $K = 0$ (b) $K > 1$

   (c) $K = 1$ (d) $K < 1$

   [NCERT Exemplar]

Ans. *(d) $K < 1$*

Explanation: ΔG° and K are related as:

$\Delta G^\circ = -RT \ln K$

When $\Delta G^\circ > 0$ means ΔG° is positive.

This can be so if the value of K is negative i.e., $K < 1$ according to the relation.

2. **Predict the Q_c value of the reaction when 0.080 M and 0.015 M of SO_2 and Cl_2 are combined to form SO_2Cl_2 of 0.200 M if $K_c = 0.078$.**

   (a) 0.03 M (b) 0.0006 M

   (c) 0.006 M (d) 0.08 M

Ans. *(c) 0.006 M*

Explanation:
$$Q_c = \frac{[SO_2][Cl_2]}{[SO_2Cl_2]}$$
$$= \frac{(0.080)(0.015)}{(0.200)}$$
$$= 0.006$$

3. **Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$?**

   (a) $\Delta G^\circ = 0$ (b) $\Delta G^\circ > 0$

   (c) $\Delta G^\circ < 0$ (d) $\Delta G^\circ = -RT \ln 2$

   [NCERT Exemplar]

Ans. *(a) $\Delta G^\circ = 0$*

Explanation: Formula used is

$$\Delta G^\circ = -RT\ln K$$

Since at half stage completion, [A] = [B]

Thus,

K = [product]/[reactant] = [B]/[A] = 1

As for 50% completion both product and reactant will have equal concentration.

$$\ln(K) = \ln(1) = 0$$
$$\therefore \quad \Delta G^\circ = -RT(0) = 0.$$

4. **In the following reaction, $PCl_{5(g)} \rightleftharpoons PCl_3 + Cl_{2(g)}$ the value of $K_p = 0.497$ and 500 K.**

   The three gases are mixed in a rigid container so that the partial pressure of each gas is initially 1atm. Which of the following statement is true regarding this?

   (a) More PCl_5 will be produced.

   (b) More PCl_3 will be produced.

   (c) Equilibrium is established when the reaction is completed.

   (d) None of the above.

Ans. *(a) More PCl_5 will be produced*

Explanation: First calculate the value of Q_p for the given reaction:

$$Q_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

$$Q_p = \frac{1 \text{ atm} \times 1 \text{ atm}}{1 \text{ atm}} = 1$$

So, here the value of $Q_p > K_p$. The reaction will go in the backward direction. Thus, more PCl_5 will be produced.

5. **For the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ at 300 K value of $\Delta G^\circ = -690.9R$. The equilibrium constant for the reaction at that temperature is:**

   (a) 10 atm^{-1} (b) 11 atm^{-1}

   (c) 10^{-1} atm (d) 10 atm

Ans. *(a) 10 atm^{-1}*

Explanation: $\Delta G^\circ = -RT \ln K$

Or
$$\Delta G^\circ = -2.303RT\log K$$
$$-690.9R = -2.303R \times 300 \log K$$
$$1 = \log K$$
$$K = 10$$

So, the value of equilibrium constant is 10 atm^{-1}.

6. The equilibrium constant of the reaction may be written as:

(a) $K = e^{-\Delta G^\circ/RT}$ (b) $K = e^{-\Delta H/RT}$

(c) $K = e^{-\Delta G/RT}$ (d) $K = e^{\Delta G^\circ/RT}$

Ans. *(a)* $K = e^{-\Delta G^\circ/RT}$

Explanation: Since $\Delta G = \Delta G^\circ + RT\ln Q_c$

At equilibrium $\Delta G = 0$ and $Q_c = K_c$

$$\Delta G^\circ = -RT\ln K_c$$

Taking antilog both sides we get:

$$K_c = e^{-\Delta G^\circ/RT}$$

7. The equilibrium is established at 300 K for the reaction: $S_{(s)} + H_{2(g)} \rightleftharpoons H_2S_{(g)}; K_p = 0.08$.

If 1 mole of both H_2 and S are heated to 300K in 1L vessel, what will be the partial pressure of H_2S at equilibrium?

(a) 1 atm (b) 1.7 atm

(c) 4.1 atm (d) 4.69 atm

Ans. *(b) 1.7 atm*

Explanation: $S_{(s)} + H_{2(g)} \rightleftharpoons H_2S_{(g)}$

$$\phantom{S_{(s)} + {}} 1-x \qquad\qquad x$$

$$K_p = \frac{[P_{H_2S}]}{[P_{H_2}]}$$

$$\Rightarrow \quad 0.08 = \frac{x}{1-x}$$

$$\Rightarrow \quad x = 0.07$$

Now partial pressure of H_2S is calculated as:

$$P_{H_2S} = \left(\frac{n_{H_2S}}{V}\right)RT$$

$$= 0.07 \times 0.082 \times 300$$

$$= 1.72 \text{ atm}$$

8. A sample of NOCl was decomposed to form 0.015 mol of Cl_2 and 4.00 mol of NO. The contents of the reactor were then analyzed and found to contain 2.01 mol of NOCl. Calculate the value of K_c.

(a) 0.5236 (b) 0.4356

(c) 0.0523 (d) 0.3122

Ans. *(a) 0.5236*

Explanation: $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

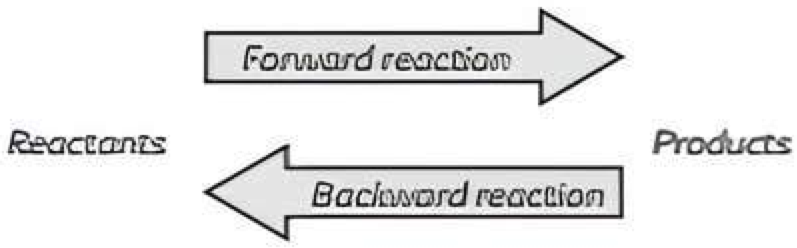
$$K_c = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$= \frac{(4)^2(0.015)}{(2.01)^2}$$

$$= 0.0544$$

Related Theory

- *A reversible reaction is one in which the reactants generate products that in turn react with each other to give the reactants back to their original state. In reversible processes, the concentrations of the reactants and products will no longer fluctuate.*



9. In the reaction; $Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-$, if the concentration of OH^- ions is decreased by 1/4 times, then the equilibrium concentration of Fe^{3+} will increase by:

(a) 8 times (b) 16 times

(c) 64 times (d) 4 times

Ans. *(c) 64 times*

Explanation: $K_c = [x][3x]^3 \quad$ — (i)

When concentration of OH^- ions is decreased by $\frac{1}{4}$ times.

$$K_c = [x'] \left[\frac{3x}{4}\right]^3 \quad \text{— (ii)}$$

Equating eqs. (i) and (ii), $K_c = [x'] \left[\frac{3x}{4}\right]^3$

$$x \times (3x)^3 = x' \left(\frac{3x}{4}\right)^3$$

$$64x = x'$$

Assertion-Reason (A-R)

In the following question no. (10-14) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

10. Assertion (A): For any chemical reaction at a particular temperature, the equilibrium constant is fixed and is a characteristic property.

Reason (R): Equilibrium constant is independent of temperature.

[NCERT Exemplar]

Ans. *(c) (A) is true but (R) is false.*

Explanation: The equilibrium constant is dependent on the temperature. It has one unique value for the particular reaction at the given temperature. Hence, the assertion is true and the reason is false.

11. Assertion(A) : If $Q_p < K_p$ reaction moves in the direction of the reactant.

Reason(R): Reaction quotient is defined in the same way as equilibrium constant at any stage of the reaction.

Ans. *(d) (A) is false but (R) is true.*

Explanation: $aX + bY \rightleftharpoons cU + dW$

$$Q_p = \frac{[U]^c[W]^d}{[X]^a[Y]^b}$$

The reaction quotient is defined in the same way as the equilibrium constant. The given assertion is wrong according to the conditions, because for the $Q_p < K_p$, reaction proceeds in the direction of the product and the reason is correct.

Related Theory

Conditions:

(1) If $Q_p > K_c$ the reaction will proceed in the reverse direction.

(2) If $Q_p < K_c$ the reaction will proceed in the forward direction.

(3) If $Q_p = K_c$ the reaction mixture is already at equilibrium.

12. Assertion (A): The Gibbs free energy for reaction is minimum at constant temperature and pressure for the reaction at equilibrium.

Reason (R): The Gibbs free energy of both the reactants and products increase and are equal at equilibrium.

Ans. *(c) (A) is true but (R) is false.*

Explanation: The Gibbs free energy is given as :
$\Delta G = \Delta G^\circ + RT\ln Q$

At equilibrium, $\Delta G^\circ = 0$ thus the value of ΔG° is minimum at this condition.

The Gibbs free energy of both the reactants and the products becomes equal at the equilibrium. They may increase or decrease also at certain conditions.

13. Assertion (A): The equilibrium constant for the given reaction is

$CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$ is

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

Reason (R): Equilibrium constant is the ratio of the product of molar concentration of the substances produced to the product of the molar concentrations of reactants with each concentration term raised to the power equal to the respective stoichiometric constant.

Ans. *(d) (A) is false but (R) is true.*

Explanation: The assertion is wrong because for the given reaction $CaCO_3$ and CaO are given as solid because the molar concentration of solids is taken as unity. Meanwhile, the given reason defines the equilibrium constant correctly.

$$K_c = [CO_2]$$

Caution

Students should always remember that molar concentration of solids and liquids are not considered for writing the K_c or Q_c of any reaction. Only gases are considered for the same.

14. Assertion (A): In the dissociation of PCl_5 at constant pressure and temperature, addition of helium at equilibrium increases the dissociation of PCl_5.

Reason (R): Helium reacts with Cl_2 and hence shifts the equilibrium in forward direction.

[NCERT Exemplar]

Ans. *(c) (A) is true but (R) is false.*

Explanation: Helium is an inert gas and hence does not react with Cl_2. However, to keep the pressure constant on addition of helium, volume of the system will increase which will favour forward reaction.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

15. *Many chemical systems, as well as physiological processes like oxygen transport by haemoglobin in blood and acid-base balance in the human body, require an understanding of equilibrium constants. The equilibrium constant of any chemical reaction is the value of its reaction quotient at chemical equilibrium, a state reached by a dynamic chemical system after a period of time has passed in which its composition shows no observable tendency to change. Equilibrium constants include stability constants, formation constants, binding constants, association constants, and dissociation constants.*

Allowing a single reaction to reach equilibrium and then measuring the concentrations of each chemical involved in that reaction yields the numerical value of an equilibrium constant. The ratio between the product and reactant concentrations is computed. Because concentrations are recorded at equilibrium, the equilibrium constant remains constant regardless of initial concentrations for a specific reaction.

(A) For the equilibrium, $PCl_5 \rightarrow PCl_3 + Cl_2$, $K_c = \alpha^2/(1-\alpha)V$. What effect does a change in volume have on the equilibrium constant for a particular reaction if the temperature remains constant?

(B) In the following equation, what change in temperature is seen to drive the reaction in the forward direction?

$I_{2(g)} \rightleftharpoons 2I_{(g)}$; ΔH° at (298K) = +250kJ

(C) Equilibrium concentration of H_2 and I_2 are heated to equilibrium in a 2 litre flask. At equilibrium, the forward and backward rate constants are found to be equal.

(i) What is the equilibrium concentration of H_2 and I_2?

(ii) What percentage of the initial concentration of H_2 has reacted at equilibrium?

Ans. (A) For the given equilibrium reaction, the K_c is the characteristic constant for the given reaction at a particular temperature. The equilibrium constant depends on the temperature only. It does not depend on the concentration or volume. So, if the temperature remains constant and the volume changes, then there will be no change in the value of K_c.

(B) $I_{2(g)} \rightleftharpoons 2I_{(g)}$; $\Delta H^\circ(298\text{ K}) = +250$ kJ

It is an endothermic reaction because the process requires heat energy from the surrounding and the value of ΔH° is positive. For the reaction to occur, the energy consumed in the reaction acts as an inclination or activation energy. As a result of this, there is a rise in temperature and hence, the reaction shifts in the forward direction.

$$\begin{array}{lccc} & H_2 & + \; I_2 & \rightleftharpoons \; 2HI \\ \text{(C) (i) Initial} & 1 & 1 & 0 \\ \text{At eq.} & 1-x & 1-x & 2x \\ & \dfrac{1-x}{2} & \dfrac{1-x}{2} & \dfrac{2x}{2} \end{array}$$

$$K = \frac{K_f}{K_b} = 1 \text{ as } K_f = K_b$$

$$1 = \frac{[HI]^2}{[H_2][I_2]}$$

$$1 = \frac{\left(\frac{2x}{2}\right)^2}{\left(\frac{1-x}{2}\right)^2}$$

$$\Rightarrow 1 = \frac{2x}{1-x}$$

$$\Rightarrow x = \frac{1}{3} = 0.33$$

Hence the equilibrium concentration for both H_2 and I_2 is $1-x$.

$\Rightarrow$ 1 − 0.33 = 0.67

(ii) If initial concentration of H_2 reacted = x.

Therefore,

$$x \times 100 = 0.33 \times 100$$
$$= 33\%$$

16. *The reaction quotient is a number in chemical thermodynamics that offers a measurement of the relative amounts of products and reactants present in a reaction mixture at a given moment in time for a reaction with well-defined overall stoichiometry. The reaction quotient is constant across time and equal to the equilibrium constant when the system is at equilibrium.*

(1) If the value of reaction quotient (Q_c) is greater than that of the equilibrium constant (K_c), the reaction tends to form more reactants.

(2) If (Q_c) is lower than (K_c), the reaction tends to form more products in order to keep the equilibrium.

(3) If (Q_c) and (K_c) are equal, then the reaction mixture is at equilibrium.

As the reaction progresses, the activities of the species, and therefore the reaction quotient, vary in a way that lowers the system's free energy. The Gibbs free energy of reaction governs the direction of change by the relation : $\Delta G = \Delta G^\circ + RT\ln Q$.

(A) The equilibrium constant K_c for the reaction $P_{4(g)} \rightleftharpoons 2P_{2(g)}$ is 1.4 at 400°C. Suppose 3 moles of P_4 and 2 moles 1 of P_2 are mixed in a 2 L container at 400°C. What is the reaction quotient Q_c?

(a) $\frac{2}{3}$ **(b) $\frac{1}{2}$**

(c) 1 **(d) 2**

(B) The ratio of equilibrium constant for the reaction and the reaction quotient is (given as $\frac{K}{Q}$) 1.33. This means that:

(a) The reaction mixture will equilibrate to form more reactant species.

(b) The reaction mixture will equilibrate to form more product species.

(c) The equilibrium ratio of reactant and product concentration will be 1.33.

(d) The equilibrium ratio of reactant and product concentration will be 0.33.

(C) Which of the following statement is incorrect?

(a) The reaction quotient is useful in predicting the volume of reaction by comparing the values of K_c and Q_c.

(b) The value of the equilibrium constant is independent of the initial and final concentration of reactants and products.

(c) Equilibrium constant is temperature dependent.

(d) If the value of $K_c > Q_c$ the reaction goes in the forward direction i.e., in the direction of products.

(D) Large value of K_c and K_p favours the product ....

(a) rarely

(b) strongly

(c) comparable

(d) does not favour the products

Ans. (A) *(a) 2/3*

Explanation: $Q_c = \frac{[P_2]^2}{[P_4]} = \frac{\left(\frac{2}{2}\right)^2}{\left(\frac{3}{2}\right)} = \frac{2}{3}$

(B) *(a) The reaction mixture will equilibrate to form more reactant species.*

Explanation:

$$\because \frac{K}{Q} = 1.33$$

$$\Rightarrow K < Q$$

This means the reaction will move in the backward direction to achieve equilibrium.

Hence, more reactants will form.

(C) *(a) The reaction quotient is useful in predicting the volume of reaction by comparing the values of K_c and Q_c.*

Explanation: The reaction quotient is useful in predicting the direction of reaction, not the volume by comparing the values of K_c and Q_c.

(D) *(b) strongly*

Explanation: Large value of K_c and K_p favours the product strongly . The values are larger than about 10^3.

17. *Le Chatelier's principle is also known as the equilibrium law, used to predict the effect of change on a system at chemical equilibrium. This principle states that equilibrium adjusts the forward and backward reactions in such a way as to accept the change affecting the equilibrium condition. When factors like concentration, pressure, temperature and inert gas that affect equilibrium are changed, the equilibrium will shift in that direction where the effects that caused by these changes are nullified. This principle is also used to manipulate reversible reactions in order to obtain suitable outcomes. Reactions proceed in both directions (reactants go to products and products go to reactants). We can tell a reaction is at equilibrium if the reaction quotient (Q) is equal to the equilibrium constant (K). We next address what happens when a system at equilibrium is disturbed so that Q is no longer equal to K. If a system at equilibrium is subjected to a perturbance or stress (such as a change in concentration) the position of equilibrium changes. Since this stress affects the concentrations of the reactants and the products, the value of Q will no longer equal the value of K. To re-establish equilibrium, the system will either shift toward the products (if Q < K) or the reactants (if Q > K) until Q returns to the same value as K.*

This process is described by Le Chatelier's principle: When a chemical system at equilibrium is disturbed, it returns to equilibrium by counteracting the disturbance. As described in the previous paragraph, the disturbance causes a change in Q; the reaction will shift to re-establish Q = K.

(A) In a vessel N_2, H_2 and NH_3 are at equilibrium. Some helium gas is introduced into the vessel so that the total pressure increases while temperature and volume remain constant. According to Le Chatelier's principle, the dissociation of NH_3:

(a) Increases

(b) Decreases

(c) Remains unchanged

(d) Equilibrium is disturbed

(B) The following reaction is at equilibrium,

$$\underset{\text{Yellow}}{Fe^{3+}_{(aq)}} + \underset{\text{Colourless}}{SCN^-_{(aq)}} \rightleftharpoons \underset{\text{Deep red}}{\left[Fe(SCN)\right]^{2+}_{(aq)}}$$

In the above reaction, colour intensity of red colour can be increased by:

(a) Addition of KSCN

(b) Addition of oxalic acid which reacts with Fe^{3+} ions.

(c) Addition of Hg^{2+} ions which react with SCN^- ions.

(d) Red colour intensity cannot be changed.

(C) The reaction

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}; K_c = 1.7 \times 10^{20}$,

will be favoured by:

(a) high temperature and low pressure

(b) low temperature and high pressure

(c) high temperature and high pressure

(d) low temperature and low pressure

(D) Which statement is incorrect about catalyst?

(a) It alters the equilibrium position in a reversible reaction.

(b) It accelerates the reaction.

(c) Its small quantity is enough to bring the considerate amount of reaction.

(d) It is unchanged at the end of reaction.

(E) The equilibrium constant for the reaction $2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$ is 4×10^{-4} at 2000 K. In presence of a catalyst, the equilibrium is attained three times faster. The equilibrium constant in the presence of the catalyst at 2000 K is:

(a) 40×10^{4}

(b) 4×10^{-4}

(c) 4×10^{-3}

(d) Difficult to compute without more data.

Ans. (A) *(c) Remains unchanged*

Explanation: Backward reaction is not favoured at high pressure.

(B) *(a) Addition of KSCN*

Explanation: Addition of KSCN increases the colour intensity of the solution as it shifts the equilibrium to right. Addition of reagents like oxalic acid or Hg^{2+} ions which remove Fe^{3+} or SCN^- ions shift the equilibrium to the left and colour intensity decreases.

(C) *(b) low temperature and high pressure*

Explanation: Since the reaction is exothermic it is favoured at low temperature. There is a decrease in the number of moles hence reaction is favoured at high pressure.

(D) *(a) It alters the equilibrium position in a reversible reaction.*

Explanation: A catalyst is a substance which speeds up the process of reaction but remains unchanged chemically at the end of reaction.

Catalyst does not alter the equilibrium position for reversible reaction.

(E) *(b) 4×10^{-4}*

Explanation: A catalyst increases the rate of forward and backward reactions by the same factor hence does not change the equilibrium constant.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

18. What do you think will happen if the equilibrium constant is greater than the reaction quotient?

Ans. If the equilibrium constant (K) is greater than the reaction quotient (Q) *i.e.*, $Q > K$ then the reaction quotient will tend to increase and the reaction will proceed in the forward direction, till the reaction reaches the equilibrium.

19. Write the correct reaction quotient expression for the reaction:

$2N_2O + O_{2(g)} \rightleftharpoons 4NO_{(g)}$

Ans. The reaction quotient expression for the given reaction is: $Q_c = \dfrac{[NO]^4}{[N_2O]^2\,[O_2]}$

20. Predict which of the following reaction will have an appreciable concentration of reactants and products:

(i) $Cl_{2(g)} \rightleftharpoons 2Cl_{(g)}, K_c = 5 \times 10^{-39}$

(ii) $Cl_{2(g)} + 2NO_{(g)} \rightleftharpoons 2NOCl_{(g)}, K_c = 3.7 \times 10^{8}$

(iii) $Cl_{2(g)} + 2NO_{2(g)} \rightleftharpoons 2NO_2Cl_{(g)}, K_c = 1.8$

[NCERT]

Ans. As for reaction given in (iii), K_c value is neither very high nor very low thus, in this reaction appreciable amount of products and reactants both will be present.

21. How can you predict the relation between the value of K_c and Q_c?

(A) If net reaction proceeds in the forward direction.

(B) If net reaction proceeds in the backward direction.

Ans. (A) $K_c > Q_c$

(B) $K_c < Q_c$

22. What effect will be seen on K_p and K_c for the reaction, $H_2 + I_2 \rightleftharpoons 2HI$ if the reaction has no change in the volume?

Ans. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$ if there is no change in the volume, then $K_p = K_c$. At constant volume, the equilibrium is not disturbed for any reaction.

23. In which case does the reaction go farthest to completion: $K = 1$, $K = 10^{10}$, $K = 10^{-10}$, and why?

Ans. The ratio of product and reactant concentration is maximum when $K = 10^{10}$ and thus reaction goes farthest to completion when $K = 10^{10}$.

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

24. Calculate the ΔG° for the conversion of oxygen to ozone, *i.e.* $\frac{3}{2}O_{2(g)} \rightleftharpoons O_{3(g)}$ at 298 K, if K_p for the conversion is 3×10^{-29}.

Ans. As we know, $\Delta G^\circ = -RT\ln K = -2.303\,RT\log K$

Therefore, $\Delta G^\circ = -2.303 \times 8.314 \times 298 \log 3 \times 10^{-29}$

$\Delta G^\circ = 162747\,\text{J mol}^{-1}$

$\Delta G^\circ = 162\,\text{kJ mol}^{-1}$

25. The value of K_c for the reaction $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$ is 1.50×10^{-40} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1×10^{-3}, what is the concentration of O_3?

Ans. The equilibrium constant expression for the given reaction can be given as:

$$K_c = \frac{[O_3]^2}{[O_2]^3}$$

$$1.50 \times 10^{-40} = \frac{[O_3]^2}{(1\times 10^{-3})^3}$$

$[O_3]^2 = (1 \times 10^{-3})^3 \times 1.50 \times 10^{-40} = 1.5 \times 10^{-49}$

Hence, the equilibrium concentration of ozone is

$[O_3] = (1.5 \times 10^{-49})^{1/2} = 1.225 \times 10^{-23}$

26. Calculate the total number of moles of reactant and product at equilibrium, if α is fraction of HI is dissociated at equilibrium in the reaction $2HI \rightleftharpoons H_2 + I_2$ and the initial moles of HI is 2 moles.

Ans.

	$2HI$	$\rightleftharpoons$	H_2	$+$	I_2
Initial moles	2		0		0
Moles at eq.	$2(1-\alpha)$		α		α

A total number of moles $= 2(1-\alpha) + \alpha + \alpha = 2$.

27. A weak acid HA is found to be 3% dissociated in 0.01M solution. Calculate the value of K_a.

Ans. $\alpha = \frac{3}{100} = 0.03$

	HA	$+$	H_2O	$\rightleftharpoons$	H_3O^+	$+$	A^-
Initial conc.	0.1				0		0
Conc. at Equilibrium	$0.1(1-0.03)$				0.1×0.03		0.1×0.03

$$\therefore K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{(0.1\times 0.03)\times(0.1\times 0.03)}{0.1(1-0.03)}$$

$$= 9.28 \times 10^{-5}$$

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

28. A mixture of 1.5 mol N_2, 2 mol H_2 and 10 mol NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.7×10^3. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Ans. The given concentration of various species is:

$[N_2] = \frac{1.50}{20}\,\text{mol L}^{-1}$ $\quad [H_2] = \frac{2}{20}\,\text{mol L}^{-1}$

$[NH_3] = \frac{10}{20}\,\text{mol L}^{-1}$

Reaction quotient Q_c is:

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

$$= \frac{\left(\frac{10}{20}\right)^2}{\left(\frac{1.50}{20}\right)\left(\frac{2}{20}\right)^3}$$

$$= 3333$$

And $\quad K_c = 1700$

Therefore, the value of K_c is not equal to Q_c the reaction mixture is not in equilibrium.

$Q_c > K_c$ So, the reaction proceeds in the reverse direction.

29. **A mixture of 1.57 mol of N_2, 1.92 mol of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?**

Ans. The reaction is :

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

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

$$= \frac{\left(\frac{8.13}{20} \text{mol} L^{-1}\right)^2}{\left(\frac{1.57}{20} \text{mol} L^{-1}\right)\left(\frac{1.92}{20} \text{mol} L^{-1}\right)^3} = 2.38 \times 10^3$$

As $Q_c \neq K_c$ the reaction mixture is not in equilibrium.

As $Q_c > K_c$ the net reaction will be in the backward direction

30. **For the reaction at equilibrium, $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$ K_p = 1.64 atm at 1000 K and 50 g of $CaCO_3$ in a 10 litres closed vessel is heated to 1000 K. What percentage of $CaCO_3$ remains unreacted at equilibrium?**

Ans. For the reaction: $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$K_c = [CO_2]$ and $K_p = P_{CO_2} = 1.64$ atm

$$\text{Number of moles of } CaCO_3 = \frac{\text{mass}}{\text{volume}} = \frac{50}{100} = 0.5$$

From ideal gas equation: $PV = nRT$

$$1.64 \times 10 = n \times 0.082 \times 1000$$

$$n = 0.2$$

Number of moles of CO_2, $n = 0.2$

Number of moles of unreacted $CaCO_3 = 0.5 - 0.2$

$= 0.3$

$$\text{Percentage of unreacted } CaCO_3 = \frac{0.3}{0.5} \times 100$$

$= 60\%$

31. **How is P related to K_p for the reaction $AB_{(g)} \rightleftharpoons A_{(g)} + B_{(g)}$ when AB is 33% dissociated at a total pressure of P?**

Ans. 33% dissociation means 0.33 moles dissociated

	$AB_{(g)}$	$\rightleftharpoons A_{(g)}$	$+ B_{(g)}$
Initial moles :	1	0	0
Eq. moles:	1–0.33 = 0.67	0.33	0.33

Total moles at equilibrium = 1.33

$$P_{AB} = \left(\frac{0.67}{1.33}\right)P$$

$$P_A = \left(\frac{0.33}{1.33}\right)P$$

$$P_B = \left(\frac{0.33}{1.33}\right)P$$

$$K_p = \frac{P_A \times P_B}{P_{AB}} = \frac{\left(\frac{0.33}{1.33}\right)P \times \left(\frac{0.33}{1.33}\right)P}{\left(\frac{0.67}{1.33}\right)P}$$

$$K_p = \frac{0.33 \times 0.33 \times P}{0.67 \times 1.33}$$

$$K_p = 0.122\,P$$

$$P = \frac{K_p}{0.122}$$

$$P = 8K_p$$

32. **The value of K_c for the reaction $2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ is 1×10^{-4}. At a given time, the composition of the reaction mixture is [HI] = 2×10^{-5} mol, $[H_2] = 1 \times 10^{-5}$ mol and $[I_2] = 1 \times 10^{-5}$ mol. In which direction will the reaction proceed?**

[NCERT Exemplar]

Ans. Given that, $K_c = 1 \times 10^{-4}$

Q_c expresses the relative ratio of products to reactants at a given instant.

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

$$= \frac{(1 \times 10^{-5})(1 \times 10^{-5})}{2 \times 10^{-5} \times 2 \times 10^{-5}}$$

$$= \frac{1}{4} = 0.25$$

Here, $Q_c > K_c$ reaction will proceed in the reverse direction.

LONG ANSWER Type Questions (LA)

[**4** & **5** marks]

33. One of the reactions that take place in producing steel from iron ore is the reduction of iron (II) oxide by carbon monoxide to give iron metal and CO_2.

$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$ $K_p = 0.30$ at 1050 K.

What is the equilibrium partial pressures of CO and CO_2 at 1050 K if the initial partial pressures are $P_{CO} = 2.0$ atm and $P_{CO_2} = 0.8$ atm.

Ans. For the reaction:

$FeO_{(s)} + CO_{(g)} \rightleftharpoons Fe_{(s)} + CO_{2(g)}$

Since $Q_p > K_p$, the reaction will go in the backward direction.

Therefore, we can say that the pressure of CO will increase while the pressure of CO_2 will decrease.

Now, let the increase in pressure of CO = decrease in pressure of CO_2. Then, we can write.

$$K_p = \frac{P_{CO_2}}{P_{CO}}$$

$$\Rightarrow \quad 0.30 = \frac{0.80 - P}{2.0 + P}$$

$$\Rightarrow \quad 0.6 + 0.30P = 0.80 - P$$

$$P = \frac{0.20}{1.30} = 0.15$$

Therefore, the equilibrium pressure of CO_2, P_{CO_2} = 0.80 − 0.15 = 0.65 atm.

The equilibrium partial pressure of CO, P_{CO} = 2.0 + 0.15 = 2.15 atm.

34. Write the relation between ΔG and Q, and define the meaning of each term and answer the following questions:

(A) Why a reaction proceeds forward when $Q < K$ and no net reaction occurs when $Q = K$?

(B) Explain the effect of an increase in pressure in terms of the reaction quotient Q. For the reaction,

$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$

[NCERT Exemplar]

Ans. The relation between ΔG and Q is:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

ΔG = change in free energy as the reaction proceeds

ΔG° = Standard free energy

Q = Reaction quotient

R = Gas constant

T = Absolute temperature in K

(A) Since, $\Delta G^\circ = -RT \ln K_c$

$$\Delta G = -RT \ln K_c + RT \ln Q_c$$

$$\Delta G = RT \ln (Q_c - K_c)$$

If $Q < K$, ΔG will be negative and the reaction proceeds in the forward direction.

If $Q = K$, $\Delta G = 0$ reaction is in equilibrium and there is no net reaction.

(B) $CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

On increasing the pressure, volume decreases. If we doubled the pressure, the volume will be halved but the molar concentration will be doubled. Then,

$$Q_c = \frac{2[CH_4]\,2[H_2O]}{2[CO]\{2[H_2]\}^3} = \frac{1}{4}\frac{[CH_4][H_2O]}{[CO][H_2]^3} = \frac{1}{4}K_c$$

Therefore, Q_c is less than K_c. So, Q_c will tend to increase to re-establish equilibrium and the reaction will go in the forward direction.

35. State and explain Le-Chatelier's principle. Explain the effect of change in concentration, pressure and temperature on the following reactions.

(A) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $\Delta H = -92.4 kJ$

(B) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, $\Delta H = -180.7 kJ$

Ans. Le Chatelier's principle is of a very general nature and can be applied to any physical or chemical system at equilibrium. To a chemical system at equilibrium, the constraint can be applied by changing the concentration of reactants or products, by changing the pressure of the system, or by changing the temperature. Therefore, for a chemical system at equilibrium, Le Chatelier's principle can be stated as when a constraint (stress) is applied on a system at equilibrium, the system behaves in such a way so as to counteract the constraint.

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

At equilibrium, the concentration of ammonia becomes constant and no more ammonia is formed. Therefore to effect the formation of more ammonia, the equilibrium must be made to shift in the forward direction. According to Le Chatelier's principle, this can be achieved either by increasing the concentration of K_2 (or H_2) or by decreasing the concentration of ammonia.

An increase in the pressure decreases the volume and hence an increases in the number of moles present in the unit volume. According to Le Chatelier's principle, the equilibrium must shift in forward direction to oppose the increase in number of moles per unit volume. Hence more nitrogen and hydrogen combine to form more ammonia.

When the temperature on this system is increased, heat is supplied to it from outside. According to Le Chatelier's principle, the equilibrium should shift in the direction which involves the absorption of the added heat. Obviously, the backward reaction is endothermic. Therefore, the equilibrium shifts from right to left, *i.e.* ammonia forward decomposes to give back N_2 and H_2. On the other hand, a decrease in temperature shifts the equilibrium towards right and more ammonia is formed. Hence, a higher yield of ammonia is possible only at low temperatures.

(B) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}, \Delta H = -180.7$ kJ

According to Le Chatelier's principle, if we increase the concentration of NO, the rate of forward reaction will increase, i.e., more NO_2 will be formed. When the concentration of any of the reactants or products is changed, the system readjusts itself by shifting the equilibrium in a direction which counteracts the change in concentration that was made.

There is no effect of increasing or decreasing the pressure on a system which involves no change in number of moles.

This reaction is endothermic in the forward direction and exothermic in the backward direction. According to Le Chatelier's principle, an increase in temperature will favour the forward reaction to occur. Therefore, at high temperature, a higher yield of nitric oxide will be obtained.

◆◆◆

ACIDS, BASES, SALTS AND IONIC EQUILIBRIA

3

TOPIC 1

IONIC EQUILIBRIUM IN SOLUTIONS

The solutions which allow the passage of current through them are known as electrolytic solutions. Such solutions consist of ions due to which they are able to conduct the electric current. The properties of an electrolytic solution are decided by the nature of ions present in it. In an electrolytic solution, there exists an equilibrium between the ions and the undissociated molecules of the substance forming the solution. This equilibrium is termed as ionic equilibrium. In the forthcoming discussion, we shall study some important topics related to ionic equilibria. We must have come across the equilibrium reaction given below which involves ions:

$$\underset{\text{(yellow)}}{Fe^{3+}_{(aq)}} + \underset{\text{(colourless)}}{SCN^{-}_{(aq)}} \rightleftharpoons \underset{\text{(deep red)}}{\left[Fe(SCN)\right]^{2+}_{(aq)}}$$

For example, Common salt (*NaCl*) is an electrolyte which in the aqueous solution gives Na^+ and Cl^- ions. Hence, it conducts electricity. Sugar is sucrose $(C_{12}H_{22}H_{11})$ which is a non-electrolyte and does not give ions in the solution. Hence, it does not conduct electricity.

Some important aspects of ionic equilibria have been discussed briefly below:

Electrolytes and Non-electrolytes

Water soluble substances can broadly be classified into following two categories.

Electrolytes

The substances which dissociate into ions in aqueous solutions are called electrolytes. These are mostly ionic compounds and possess oppositely charged ions held together by electrostatic forces of attraction. When dissolved in water, the electrostatic forces responsible for holding ions together get weakened under the influence of high dielectric constant of water and ions get separated. This process is called dissociation or ionisation. For example, sodium chloride is an electrolyte and dissociates into ions.

Polar covalent compounds may also dissociate into ions in the same way and act as electrolytes. Due to the presence of oppositely charged ions, the solution of an electrolyte conducts an electric current.

Electrolytes can further be classified into following two categories.

(1) **Strong electrolytes:** The electrolytes which are completely (or almost completely) ionised in solutions are called strong electrolytes. These are true ionic compounds and ionise to an extent of almost 100% in solution. For example, NaCl, KCl, KBr, NH_4Cl, HCl, HNO_3, H_2SO_4, etc. When 1 mole of KCl is dissolved in one litre of water, the resulting solution contains 1.0 mole of K^+ ions and 1.0 mole of Cl^- ions and practically no unionised KCl. The ions remain solvated in solution. Since the solution of a strong electrolyte possesses only a very few unionised molecules at equilibrium, the equations for ionisation reactions for strong electrolytes are written with a single arrow directed to the right as shown below.

$$KCl_{(aq)} \rightarrow K^{+}_{(aq)} + Cl^{-}_{(aq)}$$

(2) **Weak electrolytes:** The electrolytes which do not dissociate (ionise) much in solution are called weak electrolytes. These are mostly polar covalent compounds and are weakly ionised in solution. For example, CH_3COOH, NH_4OH, HCN etc. The solution of a weak electrolyte contains both the ions as well as the undissociated molecules and an equilibrium exists between them. For example,

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH^{+}_{4(aq)} + OH^{-}_{(aq)}$$

Due to the presence of an equilibrium between the undissociated molecules and ions, the equations for the dissociation of weak electrolytes are written with double headed arrows.

Ionisation of Weak Electrolytes

The weak electrolytes are partially ionised in solution. The solution of a weak electrolyte contains both the undissociated molecules as well as the ions and a dynamic equilibrium exists between them.

Let us consider the dissociation of acetic acid which is a weak electrolyte. In an aqueous solution, it dissociates (ionises) as follows:

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^{+}_{(aq)} + CH_3COO^{-}_{(aq)}$$

According to the law of equilibrium, we have

$$K = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[H_2O\right]\left[CH_3COOH\right]}$$

Where K is the equilibrium constant. Water acts as a solvent and it's concentration can be regarded as constant. Therefore, we have

$$K_a = K[H_2O] = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

Here K_a is a new equilibrium constant and is referred to as ionisation constant or dissociation constant of the acid under study. The suffix a in K_a refers to acid. We can use a suffix b in case of a base i.e., K_b.

Let us consider a general case. Suppose AB is a weak electrolyte (acid, base or a neutral compound) which when dissolved in water dissociates partially to give A^+ and B^- ions. Let c be the initial concentration of the electrolyte AB in solution and let α be its degree of dissociation. As we have seen earlier, degree of dissociation is the fraction of total number of moles which undergoes dissociation and is given by

$$\alpha = \frac{\text{Number of moles undergoing dissociation (ionisation)}}{\text{Total number of moles}}$$

Since the dissociation of an electrolyte involves the process of ionisation, the degree of dissociation may also be referred to as degree of ionisation.

Important

➥ *The process of separation of ions that are already present in the solid compound is called dissociation whereas the process of splitting of a neutral molecule into charged ions is called ionisation. However, both terms are widely used without any difference.*

TOPIC 2

ACIDS, BASES AND SALTS

The criterion for a substance to act as an acid or a base has been a matter of much discussion among the chemists. According to Boyle (1680), acids were substances that tasted sour, changed the colour of the litmus. The criterion for a substance to act as an acid or a base has been a matter of much discussion among the from blue to red and reacted with certain metals to give off hydrogen gas. Roulle (1774) regarded bases as the substances that tasted bitter, possessed detergent and soapy properties and turned red litmus blue. Lavoisier (1787) believed that the acidic properties of a substance were due to the presence of oxygen in them. However, Davy (1811) contradicted the views of Lavoisier and showed that the substances like HCl, H_2S etc., were also acids. Liebig (1938) defined acids as the compounds which contained one or more replaceable hydrogen atoms. Thus, there had been a lot of discussion over the definition of acid and base. In the forthcoming discussion, we shall study some important concepts of acid and base and will see how acid-base equilibrium is established.

Arrhenius Concept

S. Arrhenius, in 1884, defined acids and bases in terms of ions given by them. According to Arrhenius, an acid is a substance which dissociates to give H^+ ions in aqueous solution while a base is the substance which dissociates to give OH^- ions in aqueous solution.

According to this concept, substances like HCl, HNO_3, H_2SO_4, CH_3COOH, etc., are acidic because they can furnish H^+ ions in solution.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

Similarly, substances like NH_4OH, NaOH, KOH etc. are bases because they can dissociate to give OH^- ions in solution.

$$NaOH_{(aq)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

According to this concept, the acid-base neutralisation process is actually the combination of H^+ ions (given by acid) and OH^- ions (given by base) to form water molecules. For example,

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$$

Arrhenius theory beautifully explained the common acid-base reactions. However, there were several limitations of this concept also. For example, this theory did not cover several substances which acted as acids or bases but were unable to furnish H^+ or OH^- ions in solution.

Bronsted-Lowry Concept (Protonic Concept)

In 1923, J.N. Bronsted and T.M. Lowry proposed a more general concept of acids and bases. They defined acids and bases in terms of H^+ ions or protons (an H^+ ion is actually a proton). According to Bronsted and Lowry, acids are proton donors while bases are proton acceptors.

It is to be noted that an H^+ ion is simply a proton. The neutral hydrogen atom contains only one proton and one electron. H^+ ion is formed when a neutral hydrogen atom loses its electron. Therefore, what is left in the form of H^+ ion is a proton. Due to the high charge density, it should not have an independent existence. It is believed that in an aqueous solution it combines with a water molecule and forms a hydrated ion called hydronium ion (H_3O^+). This ion has an independent existence in the aqueous solution.

$$\underset{\text{Proton}}{H^+} + (H_2O) \rightarrow \underset{\text{Hydronium ion}}{H_3O^+}$$

Bronsted and Lowry's concept is a wider concept and is not restricted only to neutral molecules. Even the ions can be regarded as acids and bases in this concept. A more detailed treatment of this concept is as follows.

Acids: According to this concept the molecules, cations or anions which have a tendency to donate H^+ ions (or protons) to any other substance are acids. Thus acids can be classified into following three categories.

(1) Molecular acids: HCl, HNO_3, CH_3COOH, $HClO_4$ etc.

(2) Cationic acids: $[Fe(H_2O)_6]^{3+}$, $[Al(H_2O)_6]^{3+}$, $\left[Fe(H_2O)_6\right]^{3+}$, $[Al(H_2O)_6]^{3+}$, NH_4^+, etc.

(3) Anionic acids: NH_2^-, HCO_3^-, HS^-, HSO_4^-, $H_2PO_4^-$ etc.

All these species have a tendency to donate H^+ ions and act as acids.

Bases: According to Bronsted and Lowry, bases are those molecules, cations or anions which have a tendency to accept protons or H^+ ions from other substances.

Thus, bases are of following three types.

(1) Molecular bases: NH_3, RNH_2, C_5H_5N etc.

(2) Cationic bases: $[Al(H_2O)_5OH]^{2+}$, $[Fe(H_2O)_5OH]^{2+}$, etc.

(3) Anionic bases: Cl^-, NO_3^-, HSO_4^-, PO_4^{3-}, etc.

Conjugate pairs of acid and base

According to this concept, an acid-base reaction can be expressed as

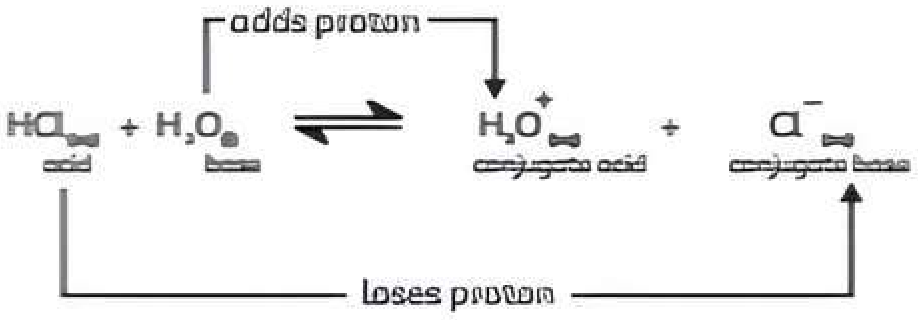
$$\text{Acid} \rightleftharpoons \text{Base} + H^+$$

Therefore, an acid and a base are related to each other. Every acid changes into a base after releasing one proton and every base on accepting a proton changes into an acid. Acids and bases thus exist in pairs and these pairs are called conjugate pairs. A conjugate pair may be termed as the chemical species that differs from the other only to the extent of transferred proton. Thus, the conjugate acid differs from its conjugate base by one proton and vice versa.

For example, let us study the following reaction.

$$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$$

In this reaction, HCl donates a proton and changes into Cl^- ion. Thus HCl is an acid and Cl^- is its conjugate base. H_2O molecule accepts the proton given by HCl and changes into H_3O^+ ion. Therefore, H_2O molecule acts as a base and H_3O^+ is its conjugate acid. Since H_3O^+ has a tendency to give a proton and Cl^- has a tendency to accept it, the exchange of proton is a reversible process. The above reaction can be written as:



Strengths of Acids and Bases

The strength of an acid is determined by its tendency to lose protons. The higher the tendency of an acid to lose the proton, the greater is its strength. Acids like HCl, HNO_3, H_2SO_4 etc. possess very high tendency to lose protons. Therefore, they are strong acids. On the other hand, acids like CH_3COOH, HCN etc. possess a little tendency to lose protons and are regarded as weak acids. The strength of a base is determined by its tendency to gain protons. The bases like CH_3COO^-, CN^-, OH^-, NH_3 etc. are strong bases because they possess very high tendency to gain protons whereas the bases like Cl^-, NO_3^-, SO_4^{2-}, etc. are weak bases because they have little tendency to accept protons.

The conjugate base of a strong acid is always a weak base and the conjugate base of a weak acid is always a strong base. For example.

$$\underset{\text{Strong acid}}{HCl_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Weak base}}{Cl^-_{(aq)}}$$

$$\underset{\text{Weak acid}}{CH_3COOH_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Strong base}}{CH_3COO^-_{(aq)}}$$

Important

- *Water-soluble organic compounds such as phenolphthalein and bromothymol blue are weak acids and have a different colour in their acid (HIn) and conjugate base (In⁻) forms, so these are widely used as indicators in acid-base titrations.*

Example 3.1: **The species H_2O, HCO_3^-, HSO_4^- and NH_3 can act both as Bronsted acids and bases. For each case give the corresponding conjugate acid and conjugate base. [NCERT]**

Ans. A conjugate base is obtained by adding a proton to species and a conjugate base is obtained by removing a proton from the given species. Thus, the corresponding conjugate acid and base for the given species are as follows

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}

Species	Conjugate acid	Conjugate base
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

Lewis Concept (Electronic Concept)

G.N. Lewis (1923) proposed a more general and more fundamental concept of acid and base in terms of electrons. This is perhaps the most widely used concept due to its simplicity and wider applications.

According to Lewis, a base is a substance which can furnish an electron pair to form a coordinate bond while acid is substance which has a tendency to accept an electron pair from a base to form a coordinate bond.

Hence, a Lewis base possesses a lone pair of electrons and acts as an electron pair donor. The Lewis acid possesses either an incomplete octet or can expand its octet and thereby acts as an electron pair acceptor species like OH^-, Cl^-, CN^-, H_2O, NH_3, ROH, RNH_2, etc. poses lone pair of electrons and behaves as Lewis bases.

Substances like SO_3, BCl_3, $AlCl_3$, BF_3 and $ZnCl_2$ are examples of Lewis acids. The central atom in the species possesses an incomplete octet and can take a lone pair of electrons.

A typical example of a Lewis acid-base reaction is as follows.

$$\underset{\substack{\text{Lewis acid}\\ \text{(electron pair}\\ \text{acceptor)}}}{BF_3} + \underset{\substack{\text{Lewis base}\\ \text{(electron pair}\\ \text{donor)}}}{NH_3} \longrightarrow \underset{\text{Complex}}{BF_3 \longleftarrow NH_3}$$

In this reaction; in the acid BF_3, the central boron atom possesses an incomplete octet and can take a lone pair of electrons whereas the nitrogen atom of base NH_3, possesses a lone pair of electrons. Therefore, the two combine together to form a complex.

Important

- *H_2O is regarded as Lewis base because it acts as an electron donor due to the presence of two lone pairs of electrons on the oxygen atom.*

Merits: Lewis concept is a very wide concept and has the following merits over other concepts.

(1) Acid-base reactions not involving protons are covered by this concept.

(2) According to this concept acid-base behaviour neither involves any particular species nor depends upon the presence or absence of a solvent.

(3) Basic properties of metal oxides and acidic properties of non-metal oxides can easily be explained on the basis of this concept.

(4) This concept includes many gas phases and high temperature non-solvent reactions as neutralisation processes.

Limitations:

(1) This concept has no uniform scale of acid-base strength. The strength of acid and base in this concept is variable and depends on the reaction selected.

(2) The concept is so broad that the terms acid and base used in general chemistry lose their original meaning and create unnecessary complications.

Example 3.2: **Which of the following are Lewis acids?**

H_2O, BF_3, H^+, NH_4^+ **[NCERT]**

Ans. Lewis acids have a tendency to accept electrons. Electron deficient or positively charged species are considered as lewis acid. BF_3, H^+ and NH_4^+ acts as Lewis acids.

Example 3.3: **Classify the following species into Lewis acids and Lewis bases and show how these act as such:**

(A) OH^- **(B) F^-**

(C) H^+ **(D) BCl_3** **[NCERT]**

Ans. (A) Hydroxyl ion acts as a Lewis base because has a tendency to donate a lone pair of electrons (OH^-).

(B) Fluoride ion acts as a Lewis base because it has a tendency to donate anyone of its four lone pairs of electrons.

(C) A proton behaves as a Lewis acid because it can accept a lone pair of electrons from bases like hydroxyl ions and fluoride ions.

(D) BCl_3 behaves as Lewis acid because it can accept a lone pair of electrons from species like ammonia or amine molecules.

OBJECTIVE Type Questions

[1 mark]

1. A 0.2 molar solution of formic acid is 3.2% ionised, its ionisation contant is:

(a) 2.1×10^{-4} (b) 1.25×10^{-6}

(c) 1.25×10^{-5} (d) 9.6×10^{-3}

Ans. *(a) 2.1×10^{-4}*

Explanation: $HCOOH + H_2O \rightarrow H_3O^+ + HCOO^-$

	$HCOOH$	H_3O^+	$HCOO^-$
Initial conc.	C	0	0
Concentration at equilibrium	$C - C\alpha$	$C\alpha$	$C\alpha$

$$K_a = \frac{(C\alpha)^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

$$C = 0.2 \text{ M}$$

$$\alpha = 3.2\% = 0.032$$

$$K_a = \frac{(0.032)^2 \times 0.2}{(1-0.032)}$$

$$K_a = 2.1 \times 10^{-4}$$

2. **K_a of 0.01M acetic acid in 0.1M HCl is 1.8×10^{-5}. Calculate the percentage of ionisation of acetic acid.**

(a) 1.8% (b) 18%
(c) 0.18% (d) 0.018%

Ans. *(d) 0.018%*

Explanation:

$$\underset{0.01(1-x)}{CH_3COOH} \rightleftharpoons \underset{0.01x}{CH_3COO^-} + \underset{0.1}{H^+}$$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{(0.01x)(0.1)}{0.01(1-x)} = 1.8 \times 10^{-5}$$

Only the H^+ ion from HCl acid is significant and $(1-x) \approx 1$. Thus,

$$0.1x = 1.8 \times 10^{-5}(1-x)$$

$$x = 1.8 \times 10^{-4}$$

Percentage ionisation = 0.018%

3. **Find the initial concentration of CH_3COOH molecule whose ionisation constant is 1.7×10^{-5} and concentration of H^+ ion is 3.4×10^{-4}.**

(a) 3.4×10^{-3} (b) 6.8×10^{-3}
(c) 3.4×10^{-4} (d) 6.8×10^{-4}

Ans. *(b) 6.8×10^{-3}*

Explanation: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

At equilibrium x 3.4×10^{-4} 3.4×10^{-4}

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.7 \times 10^{-5} = \frac{(3.4 \times 10^{-4})(3.4 \times 10^{-4})}{x}$$

$$x = 6.8 \times 10^{-3}$$

4. **What is the dissociation constant of an acid HA whose degree of ionisation is 0.00001 at 0.1 M concentration?**

(a) 10^{-7} (b) 10^{-9}
(c) 10^{-11} (d) 10^{-8}

Ans. *(c) 10^{-11}*

Explanation: The degree of ionisation of HA = 0.00001 at 0.1 M

Dissociation constant $K_a = C\alpha^2 = 0.1 \times (10^{-5})^2$
$= 10^{-11}$ at 0.1 M

5. **Which of the following is least likely to behave as Lewis acid?**

(a) NH_3 (b) H_2O
(c) OH^- (d) BF_3 [Diksha]

Ans. *(d) BF_3*

Explanation : As BF_3 can accept electrons hence it acts as an Lewis acid.

6. **Identify Bronsted Lowry Acids in the reaction:**

$$\underset{(X)}{[Al(H_2O)_6]^{3+}} + \underset{(Y)}{HCO_3^-} \rightleftharpoons \underset{(P)}{[Al(H_2O)_5(OH)]^{2+}} + \underset{(Q)}{H_2CO_3}$$

(a) X, Y (b) Y, P
(c) P, Q (d) X, Q

[Delhi Gov. QB 2022]

Ans. *(d) X, Q*

Explanation: According to Bronsted proton donors are acids while proton acceptors are bases. Hence, X is a Bronsted acid which on donating a proton coveted to a conjugate base P. Q is also an acid as it is the conjugate acid of base Y.

Assertion-Reason (A-R)

In the following question no. (7-9) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

7. **Assertion (A): Weak acids have very strong conjugate bases while strong acids have weak conjugate bases.**

Reason (R): Conjugate acid – base pairs differ only by one proton.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Strong acids such as perchloric acid and hydrochloric acid give conjugate base ions ClO_4^-, Cl^- which are much weaker bases than H_2O. On the other hand, a weak acid like acetic acid is only partially dissociated in an aqueous medium and thus the solution mainly contains undissociated acetic acid which proves that CH_3COO^- is a stronger base than H_2O.

Related Theory

- *Some substances exhibit dual behaviour. i.e. they behave as acid and base both. Such substances are called amphoteric or amphiprotic substances.*

8. **Assertion (A): The ionisation constants of weak diprotic acid are in the order of $K_{a_1} > K_{a_2}$.**

Reason (R): Removal of H^+ from anion is difficult as compared to neutral atoms. [Delhi Govt.]

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: The ionisation constants of weak diprotic acid are in order of $K_{a_1} > K_{a_2}$. due to more stability of conjugate base and removal of H^+ from anion is difficult as compared to neutral atom.

9. **Assertion (A): The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.**

Reason (R): Hydrogen sulphide is a weak acid.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: Ionisation of H_2S gets suppressed in water due to common H^+ ions produced by HCl.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

10. *An acid-base reaction is a chemical reaction that occurs between an acid and a base. Several concepts exist that provide alternative definitions for the reaction mechanisms involved and their application in solving related problems. Despite several differences in definitions, their importance as different methods of analysis becomes apparent when they are applied to acid-base reactions for gaseous or liquid species, or when acid or base character may be somewhat less apparent.*

The Arrhenius definition of acid-base reactions, which was devised by Svante Arrhenius, is a development of the hydrogen theory of acids. It was used to provide a modern definition of acids and bases, and followed from Arrhenius's work with Friedrich Wilhelm Ostwald in establishing the presence of ions in an aqueous solution in 1884. This led to Arrhenius receiving the Nobel Prize in Chemistry in 1903. As defined by Arrhenius:

- *An Arrhenius acid is a substance that dissociates in water to form hydrogen ions(H^+). In other words, an acid increases the concentration of H^+ ions in an aqueous solution. This protonation of water yields the hydronium ion (H_3O^+); in modern times, H^+ is used as a shorthand for (H_3O^+) because it is now known that a bare proton (H^+) does not exist as a free species in aqueous solution.*
- *An Arrhenius base is a substance that dissociates in water to form hydroxide(OH^-) ions. In other words, a base increases the concentration of (OH^-) ions in an aqueous solution.*

(A) Comment on the statement: All Arrhenius acids are Bronsted acids but all Arrhenius bases may not be Bronsted bases.

(B) Why heat of neutralisation for a strong acid and strong base is always constant?

(C) Give two limitations of Arrhenius's theory?

Ans. (A) The statement is true. In the Arrhenius concept as well as in the Bronsted concept, an acid is regarded as a substance which can give an H^+ ion or proton. Therefore, all Arrhenius acids are Bronsted acids. On the other hand, the definitions of base are different in the two concepts. In Arrhenius's concept, a base is regarded as a substance which gives OH^- ions in solution whereas a Bronsted base is a proton acceptor. Hence, Arrhenius bases may not be Bronsted bases. For example, NaOH can give OH^- ions but cannot accept a proton. Hence, NaOH is an Arrhenius base but not a Bronsted base.

(B) Heat of neutralisation is always constant for a strong acid and strong base because they are completely ionised in dilute solution.

(C) Limitations of Arrhenius's theory are:

(1) It only applies to substances that produce hydrogen ions (H^+) or hydroxide ions (OH^-).

(2) Arrhenius did not explain in his theory the behaviour of acids and bases in a non-aqueous solution.

11. *A very strong base would give a very weak conjugate acid. A weak acid HA is only partially* *dissociated in an aqueous medium and thus, the solution mainly contains undissociated HA molecules. Example: HCl is a strong acid. If HCl is a strong acid, it must be a good proton donor. HCl can only be a good proton donor, however, if the Cl^- ion is a poor proton acceptor. Thus, the Cl^- ion must be a weak base. Strong acid-like perchloric acid, hydrochloric acid will release conjugate base ions ClO_4^-, Cl^- these are weaker bases than water. Similarly, a very strong base would give a very weak conjugated acid. On the other hand, a weak acid say HA is only partially dissociated in an aqueous medium and the solution mainly contains undissociated HA molecules. The value of K_a for an acid can be used to decide whether it is a strong acid or a weak acid, in an absolute sense. It can also be used to compare the relative strengths of a pair of acids.*

(A) Common ion effect can be used in which of the following cases:

(a) Cloth making

(b) Alcohol purification

(c) Quantitative analysis

(d) Qualitative analysis

(B) The K_w is equilibrium dependent upon:

(a) temperature

(b) pressure

(c) volume

(d) concentration of acid or base

(C) Choose the correct option for a weak acid.

(a) HF **(b) CH_3COONa**

(c) Na_2CO_3 **(d) H_2S**

(D) Which of the following is the strongest conjugate base?

(a) F^- **(b) Cl^-**

(c) I^- **(d) Br^-**

(E) Among following the one pair that does not act as conjugate acid-base pair is:

(a) H_2O, H_3O^+ **(b) HCO_3^-, H_2CO_3**

(c) HSO_4^-, H_2SO_4 **(d) $NH_4^+ \text{-} NH_2^-$**

[Delhi Gov. QB 2022]

Ans. (A) *(d) Qualitative analysis*

Explanation: Common ion effect is used in the purification of common salt, qualitative analysis. In the qualitative analysis, Ammonium hydroxide is added in the presence of ammonium chloride to avoid the precipitation of V group radicals.

(B) *(a) temperature*

Explanation: The value K_w is an equilibrium constant, therefore it is temperature-dependent.

(C) *(a) HF*

Explanation: In HF, hydroxonium ion is attached to the fluoride ion, it is not free to function as an acid, thus limiting the strength of HF in water.

(D) *(a) F^-*

Explanation: The stronger the acid, the weaker will be its conjugate base.

Order of acidic nature: HI > HBr > HCl > HF

Conjugate base strength order:

$$F^- > Cl^- > Br^- > I^-$$

(E) *(d) NH_4^+, NH_2^-*

Explanation: NH_4^+ and NH_3 are conjugate acid-base pair, not NH_4^+, NH_2^-

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

12. What is the name of the compound formed by the reaction between the Lewis acid and Lewis base. [Diksha]

Ans. A coordinate compound between Lewis acid and Lewis base is formed which is called Lewis acid–base adduct.

13. Why is ammonia termed as a base though it does not contain OH^- ions?

Ans. The basic nature of ammonia is due to its tendency to donate electron pairs. Therefore, it is a Lewis base.

Caution

➥ Sometimes students get confused between Lewis acid and Lewis base. Lewis acids have a tendency to accept electrons and lewis bases have a tendency to donate electrons.

14. Concentration of $HCOO^-$ at 27°C is 10^{-3} M in pure HCOOH liquid. Find out the self-ionization constant at 27°C.

Ans. $2HCOOH \rightarrow HCOOH_2^+ + HCOO^-$

At equilibrium the concentration of $HCOOH_2^+$ and $HCOO^-$ are the same. So,

$$[HCOOH_2^+] = [HCOO^-] = 10^{-3} M$$

$$K = [HCOOH_2^+][HCOO^-] = 10^{-3} \times 10^{-3} = 10^{-6}$$

15. Write down the conjugate acid and conjugate base of H_2O, HSO_4^- and NH_3. [Diksha]

Ans. H_3O^+/OH^-, H_2SO_4/SO_4^{2-}, NH_4^+/NH_2^-

16. SO_3^{2-} is Bronsted base or acid and why?

Ans. SO_3^{2-} is an anion which can easily accept a proton thus it is Bronsted base. It cannot be a Bronsted acid as it does not have a proton to donate.

SHORT ANSWER Type-I Questions (SA-I)

[**2** marks]

17. **At 298 K, 0.01 M solution of ammonium hydroxide is 4.2% ionised. Calculate the ionisation constant of the base.**

Ans. In the present case

$$C = 0.01\text{M}\ \alpha = \frac{4.2}{100} = 0.042$$

Ammonium hydroxide ionises as

	$NH_4OH_{(aq)}$ $\rightleftharpoons$	$NH_{4(aq)}^{+}$ +	$OH_{(aq)}^{-}$
Initial conc.	0.010	0	0
Concentration at equili	0.01 (1–0.042)	0.01x 0.042	0.01x 0.042

Hence, according to the law of equilibrium

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{(0.01\times0.042)\times(0.01\times0.042)}{0.01(1-0.042)}$$

$$= \frac{0.01(0.042)^2}{1-0.042}$$

$$= 1.84 \times 10^{-5}$$

18. **The ionisation constant of HF, HCOOH and HCN at 298 K are 6.8 × 10^{-4}, 1.8 × 10^{-4} and 4.8 × 10^{-9} respectively. Calculate the ionisation constants of the corresponding conjugate base.**

Ans. $K_b = \frac{K_w}{K_a}$

For F$^-$, $K_b = \frac{10^{-14}}{6.8\times10^{-4}}$

For HCOO$^-$, $K_b = \frac{10^{-14}}{1.8\times10^{-4}} = 5.6\times10^{-11}$

For CN$^-$, $K_b = \frac{10^{-14}}{4.8\times10^{-9}} = 2.08\times10^{-6}$

19. **The ionisation of hydrochloric in water is given below:**

$HCl_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + Cl^-_{(aq)}$

Label two conjugate acid-base pairs in this ionisation. [NCERT Exemplar]

Ans. Acid – HCl (proton donor) : Conjugate base (Cl$^-$)

Base—H_2O (proton acceptor) : Conjugate acid (H_3O^+)

SHORT ANSWER Type-II Questions (SA-II)

[**3** marks]

20. **Calculate the degree of ionisation and concentration of $[H_3O^+]$ of a 0.15 M CH_3COOH solution. The dissociation constant of acetic acid is 1.8 × 10^{-5}.**

Ans. The ionisation of acetic acid in water can be represented as

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

Let α be the degree of ionisation of the given acid. For every mole of acetic acid, α moles of it will dissociate to give α moles of H_3O^+ and α moles of CH_3COO^-. Therefore, for the given concentration i.e., we have

	$CH_3COOH + H_2O \rightleftharpoons$	H_3O^+ +	CH_3COO^-
Initial conc.	0.15	0	0
Conc. at equilibrium	0.15(1 – α)	0.15 α	0.15 α

According to the law of equilibrium,

$$K_a = \frac{[H_3O^+_{(aq)}][CH_3COO^-_{(aq)}]}{[CH_3COOH_{(aq)}]}$$

Or $1.8\times10^{-5} = \frac{0.15\alpha\times0.15\alpha}{0.15(1-\alpha)} = \frac{0.15\alpha^2}{1-\alpha}$

Since, acetic acid is a very weak electrolyte, (1 – α) can be taken approximately equal to 1. Therefore, we have

$1.8 \times 10^{-5} = 0.15\alpha^2$

Or $$\alpha = \left(\frac{1.8\times10^{-5}}{0.15}\right)^{1/2} = 1.09\times10^{-2}$$

The concentration of at equilibrium

$$[H_3O^+] = 0.15 \times \alpha = 0.15 \times 1.09 \times 10^{-2}$$

$$= 1.63 \times 10^{-3}\ \text{mol L}^{-1}$$

21. **The dissociation constant of HCN is 7.24 × 10^{-10}. Calculate its degree of dissociation in 0.01 M solution.**

Ans. Suppose the degree of dissociation of HCN is α.

	$HCN + H_2O \rightleftharpoons$	H_3O^+ +	CN^-
Initial moles	0.01	0	0
Moles at	0.01(1 – α)	0.01α	0.01α

Equilibrium

Therefore, at equilibrium

$[HCN] = 0.01\ (1 - \alpha) = 0.01\ mol\ L^{-1}$

(as α is small)

$[H_3O^+] = 0.01\ \alpha\ mol\ L^{-1}$

$[CN^-] = 0.01\ \alpha\ mol\ L^{-1}$

According to the law of equilibrium,

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

Or $$7.24 \times 10^{-10} = \frac{(0.01\alpha)(0.01\alpha)}{0.01}$$

$$= 0.01\ \alpha^2$$

Or $$\alpha = \left(\frac{7.24 \times 10^{-10}}{0.01}\right)^{1/2}$$

$$= 2.69 \times 10^{-4}$$

$$\therefore \quad [H_3O^+] = \alpha \times 0.01$$

$$= 2.69 \times 10^{-4} \times 0.01$$

$$= 2.69 \times 10^{-6}\ mol\ L^{-1}$$

22. Find out the ionisation constant of 0.1 M solution of acetic acid which is 1.34% ionised at 298 K.

(Degree of dissociation = 0.0134)

Ans. $\alpha = 0.0134,\ C = 0.1M$

	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	$+ H^+$
Initial conc.	C		0	0
At equilibrium	$C - C\alpha$		$C\alpha$	$C\alpha$

$$\therefore \quad K = \frac{\alpha^2 C^2}{(1-\alpha)C}$$

$$= \frac{\alpha^2 C}{(1-\alpha)}$$

$$= \frac{(0.0134)^2 \times 0.1}{1 - 0.0134}$$

$$= 1.82 \times 10^{-5}$$

LONG ANSWER Type Questions (LA)

[4 & 5 marks]

23. (A) What is protonic concept of acids and bases?

(B) How is this concept useful in determining the relative strength of acids and bases?

Ans. (A) Bronsted and Lowry's concept of acids and bases is called protonic concept of acids and bases. Bronsted and Lowry defined acids and bases in terms of H^+ ions or protons. According to Bronsted and Lowry, acids are hydrogen ions or proton (H^+) donors while bases are hydrogen ion or proton (H^+) acceptors. According to this theory, the molecules, cations or anions which have a tendency to donate H^+ ions are acids. Thus acids can be classified into following three categories. For example, CH_3COOH, $[Al(H_2O)_6]^{3+}$, NH_2^- etc. According to this concept bases are those molecules, cations or anions which have a tendency to accept protons or H^+ ions. For example, NH_3, $[Fe(H_2O)_5\ OH]^{2+}$, PO_4^{3-} etc.

(B) According to this theory, acids which possess a very high tendency to lose protons has greater strength. Therefore, they are strong acids. For example HCl, HNO_3, H_2SO_4 etc. On the other hand, acids which possess little tendency to lose protons and are regarded as weak acids. For example, CH_3COOH, HCN etc. The bases which possess a very high tendency to gain protons are strong bases. For example, CH_3COO^-, CN^-, OH^-, NH_3, etc. While the bases which possess little tendency to accept protons are weak bases. For example, Cl^-, NO_3^-, SO_4^{2-}, etc.

The conjugate of a strong acid is always a weak base and the conjugate of a weak acid is always a strong base. For example,

$$\underset{\text{Strong acid}}{HCl_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Weak base}}{Cl^-_{(aq)}}$$

$$\underset{\text{Weak acid}}{CH_3COOH_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Strong base}}{CH_3COO^-_{(aq)}}$$

24. The ionisation constant of propanoic acid is 1.32 × 10^{-15}. Calculate the degree of ionisation if its solution is 0.05 M. What will be its degree of ionisation if the solution is 0.01 M in HCl solution?

Ans. (A) Let the degree of ionisation of propanoic acid be α.

Then, representing propionic acid as HA, we have:

HA +	H_2O	$\leftrightarrow$	H_3O^+	+	A
$(0.5 - 0.0\alpha) \approx 0.5$			0.05α		0.05α

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$= \frac{(0.5\alpha)(0.5\alpha)}{0.05} = (0.05\alpha)^2$$

$$\alpha = \frac{\sqrt{K_a}}{0.05} = 1.63 \times 10^{-3}$$

Then $[H_3O^+] = 0.05\alpha = 0.05 \times 1.63 \times 10^{-3}$

$= 8.15 \times 10^{-4}$ M

(B) In the presence of 0.1M of HCl let α′ be the degree of ionisation.

Then $[H_3O^+] = 0.01$

$[A^-] = 0.05\alpha'$

$$K_a = \frac{[CH_3CH_2COO^-][H^+]}{CH_3CH_2COOH}$$

$$1.32 \times 10^{-5} = \frac{C\alpha(0.01)}{0.05-\alpha}$$

$$C\alpha = \frac{1.32\times10^{-5}(0.05-\alpha)}{0.01}$$

$= 6.60 \times 10^{-5}$

Degree of ionisation

$$= \frac{6.60\times10^{-5}}{0.05}$$

$= 1.32\times10^{-3}$

SOLUBILITY EQUILIBRIA 4

TOPIC 1

IONISATION OF ACIDS AND BASES

The Ionisation Constant of Water and its Ionic Product

Water has a distinctive property that it can act as acid as well as base. In the acidic nature the HA will take the proton while in its basic nature, it gives the proton. Therefore, in the pure state of water, in a similar time molecules of H_2O it gives the proton and appears as acid on the other hand it takes proton it appears as basic.

Example.

$$\underset{\text{Acid}}{H_2O_{(l)}} + \underset{\text{Base}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conjugated acid}}{H_3O^+_{(aq)}} + \underset{\text{Conjugated base}}{OH^-_{(aq)}}$$

Therefore the dissociation constant

$$K = [H_3O^+]\,[OH^-] / [H_2O]$$

$$K[H_2O] = K_w = [H_3O^+]\,[OH^-]$$

K_w = ionic product of water

The concentration of H^+ or H_3O^+ ions at 298 K is 1.0×10^{-7}M which has been found experimentally. During the water molecule dissociation, it supplies the same amount of H^+ and OH^- ions, therefore the hydroxyl ions concentration is $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M

At 298 K the value of K_w

$$K_w = [H_3O^+]\,[OH^-] = (1.0 \times 10^{-7})^2 = 1.0 \times 10^{-14} M^2$$

Important

- *As K_w is an equilibrium constant therefore it is temperature dependent.*

To differentiate the acidic, neutral and basic aqueous solutions through concentration of OH^- and H_3O^+:

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic: $[H_3O^+] < [OH^-]$

The pH Scale

The concentration of hydrogen ions is calculated through pH scale. pH is defined as the logarithm of reciprocal of the concentration of hydrogen ions or negative logarithm of the concentration of hydrogen ions.

In dilute solutions (< 0.01M), activity of hydrogen ion $[H^+]$ is equal in the magnitude to molar concentration represented by $[H^+]$.

$$a_{H_3O^+} = [H^+]\ \text{mol}\,L^{-1}$$

$$pH = -\log a_{H_3O^+} = -\log \{[H^+]\ \text{mol}\,L^{-1}\}$$

$a_{H_3O^+}$ = active hydrogen atom

Thus, an acidic solution of HCl (10^{-2}M) will have a pH = 2. For the basic solution of NaOH having $[OH^-] = 10^{-4}$ M and $[H_3O^+] = 10^{-10}$ will have pH = 10. At 25°C, pure water has a concentration of hydrogen ions, $[H^+] = 10^{-7}$M, hence for the pure water

$$pH = -\log (10^{-7}) = 7$$

Acidic solution contains concentration of hydrogen ion $[H^+] > 10^{-7}$, while the basic solution contains concentration of hydrogen ions, $[H^+] < 10^{-7}$.

Differentiation of acid, base, and neutral solution according to the pH scale

(1) Acidic solution has pH<7

(2) Basic solution has pH>7

(3) Neutral solution has pH=7

Now, at 298 K

$$K_w = [H_3O^+]\,[OH^-] = 10^{-14}$$

$$-\log K_w = -\log \{[H_3O^+]\,[OH^-]\} = -\log 10^{-14}$$

$$pK_w = pH + pOH = 14$$

pK_w changes with temperature. The variation in pH with temperatures are minimal, we often ignore.

pK_w is a very important quantity for aqueous solution and controls the relative concentration of hydrogen and hydroxyl ions as their product is a constant.

Important

- *K_w of water $= [H_3O^+]\,[OH^-]$*
  $= 1.00 \times 10^{-14}\ mol^2\ dm^{-6}$
  pK_w of water = 14

Table : The pH of some common substances

Solution	pH
Saturated solution of NaOH	– 15
0.1 M NaOH solution	13
Lime water	10.5
Milk of Magnesia	10
Egg white, seawater	7.8
Human blood	7.4
Milk	6.8
Human Saliva	6.4
Black Coffee	5.0
Tomato juice	– 4.2
Soft drinks and vinegar	– 3.0
Lemon juice	– 2.2
Gastric juice	– 1.2
1 M HCl solution	– 0
Concentrated HCl	– 1.0

Example 4.1: **Case Based:**

We all get teeth at some part of our life because of our food lifestyle. When we have sugary food, the tooth begins to decay due to the presence of bacteria in the mouth, and this bacterium leads to the formation of acid, and the enamel which is the outer covering of the tooth starts to be degraded. The tooth begins to degrade when the pH level is lower than 5.5. Even though the saliva is slightly alkaline which helps to neutralize the acid present in the mouth. However, if its large amount of acids is present then saliva will not be helpful. The greater amount of acid can be removed by alkaline toothpaste. Therefore, cleaning the tooth daily helps to reduce decay.

(A) Which of the following substances leads to the formation of plaque?

(a) Acid	**(b) Bacteria**
(c) Fungi	**(d) Both (a) and (b)**

(B) What is the pH level of the antacids solution?

(a) < 9.5	**(b) > 7.0**
(c) > 14	**(d) > 9.5**

(C) Why in the old day's people used brushes with neem sticks?

(D) Define pH.

(E) Assertion (A): When the pH is lower than the tooth begins to degrade.

Reason (R): When the bee stings, it left acid in that area which causes irritation and pain.

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).

(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).

(c) (A) is true but (R) is false.

(d) (A) is false but (R) is true.

Ans. **(A)** *(d) Both (a) and (b)*

Explanation: The acid and bacteria cause the formation of plaque as it decreases the level of pH which leads to acid in the mouth which is favourable for the growth of plaque.

(B) *(b) > 7.0*

Explanation: Acidic food and drinks result in the degradation of the tooth. Hence the pH value of acid is lesser than 7.

(C) The presence of alkaline juice in the neem stick prevents the tooth from decaying.

(D) It is the negative logarithm of the concentration of hydrogen ions.

(E) *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: The lesser pH (5.5) in the mouth makes the perfect environment for the growth of bacteria which makes the tooth degrade. As the bee sting releases methanoic acid /formic acid which cause pain and irritations.

Example 4.2: **Calculate the pH of 2 g TlOH dissolved in water to give two litres of the solution.** **[NCERT]**

Ans. Molar conc. of TlOH

$$= \frac{2\,g}{(204+16+1)\,g\,mol^{-1}} \times \frac{1}{2L}$$

$$= 4.25 \times 10^{-3}\,M$$

$$[OH^-] = [TlOH] = 4.52 \times 10^{-3}$$

$$[H^+] = \frac{10^{-14}}{4.52 \times 10^{-3}} = 2.21 \times 10^{-12} M$$

$$pH = -\log(2.21 \times 10^{-12}) = 12 - (0.3424)$$

$$= 11.66$$

Related Theory

- *pH does not have any S.I. unit.*

Ionisation Constants of Weak Acids

$$\begin{array}{lcccc} & HX_{(aq)} + H_2O_{(l)} & \rightleftharpoons & H_3O^+_{(aq)} & + X^-_{(aq)} \\ \text{Initial conc.} & c & & 0 & 0 \\ & C(1-\alpha) & & C\alpha & C\alpha \end{array}$$

$$K_a = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

K_a = dissociation or ionisation constant.

The K_a does not have dimension quantity.

In the case of pH scale:

$$pK_a = -\log(K_a)$$

Important

➥ *When the value of K_a is greater the strength of the acid also increases, which means the strength of the acid depends upon K_a*

Table: The ionisation constant of some selected weak acids (at 298 K)

Acid	Ionisation Constant, K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Formic Acid (HCOOH)	1.8×10^{-4}
Niacin ($C_5H_4NO_2$)	1.5×10^{-5}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.5×10^{-5}
Hypochlorous Acid (HClO)	3.0×10^{-8}
Hydrocyanic Acid (HCN)	4.9×10^{-10}
Phenol (C_6H_5OH)	1.3×10^{-10}

Example 4.3: The ionisation constant of HF is 3.2×10^{-4}. Calculate the degree of dissociation of HF in its 0.02M solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH. [NCERT]

Ans. Proton transfer reaction:

$$HF + H_2O \rightleftharpoons H_3O^+ + F^-$$

$$K_a = 3.2 \times 10^{-4}$$

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-; K_w = 1.0 \times 10^{-14}$$

$K_a >> K_w$ there the principal reaction will be

$$\begin{array}{lcccc} & HF + H_2O & \rightleftharpoons & H_3O^+ & + \quad F^- \\ \text{Initial} & 0.02 & & 0 & 0 \\ \text{At eq.} & 0.02 - 0.02\alpha & & 0.02\alpha & 0.02\alpha \end{array}$$

In the principal reaction replace the equilibrium reaction with an equilibrium constant.

$$K_a = \frac{(0.02\alpha)^2}{(0.02 - 0.02\alpha)}$$

$$= \frac{0.02\alpha^2}{(1-\alpha)} = 3.2 \times 10^{-4}$$

Two values of the root are formed.

$$\alpha^2 = 1.6 \times 10^{-3} - 1.6 \times 10^{-2}\alpha$$

$$\alpha = +0.12 \text{ and } -0.12$$

However, we cannot accept the negative root, therefore,

$\alpha = 0.12$, this is the degree of ionisation.

Now, we will find the equilibrium concentration of: H_3O^+, F^- and HF.

$$[H_3O^+] = [F^-] = C\alpha = 0.02 \times 0.12$$

$$= 2.4 \times 10^{-3}\ M$$

$$[HF] = C(1-\alpha) = 0.02\ (1-0.12)$$

$$= 17.6 \times 10^{-3} M$$

$$pH = -\log[H^+] = -\log(2.4 \times 10^{-3}) = 2.62$$

Ionisation of Weak Bases

Equation of ionisation of weak bases are

$$MOH_{(aq)} \rightleftharpoons M^+_{(aq)} + OH^-_{(aq)}$$

$$K_b = [M^+][OH^-]/[MOH]$$

K_b = base ionisation constant

$$K_b = (C\alpha)^2 / C(1-\alpha) = C\alpha^2/(1-\alpha)$$

In the case of pH scale:

$$pK_b = -\log(K_b)$$

Table: The value of the ionisation constant of weak bases at 298 K

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-6}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Quinine, (A plant product)	1.10×10^{-6}
Pyridine, C_5H_5N	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $C_6H_5NH_2$	1.3×10^{-14}

Example 4.4: The pH of 0.05M codeine solution is 9.95. Calculate the ionisation constant and pK_b. [NCERT]

Ans. $Cod + H_2O \rightleftharpoons CodH^+ + OH^-$

$$pH = 9.95$$

$$pOH = 14 - 9.95 = 4.05$$

$$-\log[OH^-] = 4.05$$

$$-\log[OH^-] = 4.05$$

$$[OH^-] = 8.913 \times 10^{-5} M$$

$$K_b = \frac{[CodH^+][OH^-]}{[Cod]} = \frac{[OH^-]^2}{[Cod]} = \frac{(8.91 \times 10^{-5})^2}{5 \times 10^{-2}}$$

$$= 1.588 \times 10^{-4}$$

$$pK_b = -\log(1.588 \times 10^{-6}) = 6 - 0.1987$$
$$= 5.8$$

Relation between K_a and K_b

For the net reaction, we get an equilibrium constant by adding two or more than two reactions which will be similar to the equilibrium constant product for the independent reaction

$$K_{net} = K_1 \times K_2 \_\_\_\_\_$$

In the pair of conjugate acid-base $K_a \times K_b = K_w$

$$\text{In } B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiply and divided the above expression by $[H^+]$, then

$$K_b = [BH^+][OH^-][H^+] / [B][H^+]$$
$$= [OH^-][H^+]\}\{[BH^+] / [B][H^+]]$$
$$= K_w / K_a$$
$$K_a \times K_b = K_w$$

If we take the negative logarithm of both sides of the equation, then values of the conjugate acid and base are related to each other by the equation:

$$pK_a + pK_b = pK_w = 14 \text{ (at 298 K)}$$

Important

➥ *A strong acid will contain a weak conjugate base and a strong base will contain weak conjugate acid.*

Di and Polybasic Acids and Di and Polyacidic Bases

Certain acid which has more than one ionisable proton per molecule is known as di and poly basic acids.

For example, oxalic acid, sulphuric acid, phosphoric acid.

The ionisation for a dibasic acid can be:

$$H_2X_{(aq)} \rightleftharpoons H^+_{(aq)} + HX^-_{(aq)}$$
$$HX^-_{(aq)} \rightleftharpoons H^+_{(aq)} + X^{2-}_{(aq)}$$

Their equilibrium constant

$$K_{a_1} = \frac{[H^+][HX^-]}{[H_2X]}$$

$$K_{a_2} = \frac{[H^+][X^{2-}]}{[HX^-]}$$

K_{a_1} and K_{a_2} are known as 1st and 2nd ionisation constant.

$K_{a_1} > K_{a_2}$ for dibasic acids.

Diprotic acids: Acids that contain two ionisable hydrogen ions. For example $H_2SO_{4(aq)}$

Triprotic acids: Acids that contain three ionisable hydrogen ions. For example, $H_3PO_{4(aq)}$. All polyprotic acids except sulphuric acid are weak.

Important

➥ *The higher order ionisation constants (K_{a_2}, K_{a_3}) are smaller than the lower order of ionisation constant (K_{a_1}) of a polyprotic acid.*

Table: The ionisation constants of some common polyprotic Acids (298 K)

Acid	Formula	K_{a_1}	K_{a_2}	K_{a_3}
Oxalic acid	$H_2C_2O_{4(aq)}$	5.4×10^{-2}	5.4×10^{-5}	–
Ascorbic acid	$H_2C_6H_6O_{6(aq)}$	7.9×10^{-5}	1.6×10^{-12}	–
Sulfuric acid	$H_2SO_{4(aq)}$	Very large	1.0×10^{-2}	–
Hydrosulfuric acid	$H_2S_{(aq)}$	1.1×10^{-7}	1.3×10^{-13}	–
Phosphoric acid	$H_3PO_{4(aq)}$	7.1×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid	$H_3AsO_{4(aq)}$	5×10^{-3}	8×10^{-8}	4.0×10^{-13}
Carbonic acid	$H_2CO_{3(aq)}$	4.4×10^{-7}	4.7×10^{-11}	–

Factors Affecting Acids Strength

(1) The decreasing order of H – *A* bond

$$\xrightarrow{\text{Size increases}}$$
$$HF << HCl << HBr << HI$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

The H–A bond will be stronger acid when the energy needed to spilt the bond is less. As we go down to the group the size of the *A* increases. Thus, decrease in the strength of *H–A* bond. Therefore, the strength of the acid is greater.

(2) When the electronegativity of *A* is higher, then the acid strength will be more in a period.

$$\xrightarrow{\text{Electronegativity of } A \text{ increases}}$$
$$CH_4 < NH_3 < H_2O < HF$$
$$\xrightarrow[\text{Acid strength increases}]{}$$

Common Ion Effect in the Ionisation of Acids and Bases

A weak electrolyte and a strong electrolyte are put in the aqueous solution; these electrolytes will have a common ion in the weak electrolyte than the weak electrolyte dissociation decline or subdue. This suppression of weak electrolytes is known as the common ion effect.

In order to evaluate the pH of the solution resulting on addition of 0.05M acetate ion to 0.05M acetic acid solution, let's consider the acetic acid dissociation equilibrium.

$$HAc_{(aq)} \rightleftharpoons H^+_{(aq)} + Ac^-_{(aq)}$$

Initial concentration (M) 0.05 0 0.05

Let *x* be the extent of ionisation of acetic acid.

Change in concentration (M) 0.05–x x 0.05+x

Therefore,

$$K_a = \frac{[H+][Ac^-]}{[HAc]} = \frac{\{(0.05 + x)(x)\}}{(0.05)}$$

As K_a is small for weak acid $x << 0.05$

Hence $(0.05 + x) = (0.05 - x) = 0.05$

Thus

$$1.8 \times 10^{5} = (x)(0.05 + x) / (0.05 - x)$$

$$= x\,(0.05) / (0.05)$$

$$x = [H^+] = 1.8 \times 10^{-5}\ M$$

$$pH = -\log(1.8 \times 10^{-5}) = 4.74$$

Example 4.5: **Calculate the pH of a 0.10M ammonia solution. Calculate the pH after 50.0 mL of this solution is treated with 25.0 mL of 0.10M HCL The dissociation constant of ammonia, $K_b = 1.77 \times 10^{-5}$.**

Ans. $NH_3 + H_2O \leftrightarrow NH^{4+} + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.77 \times 10^{-5}$$

Before neutralisation $[NH_4^+] = [OH^-] = x$

$$[NH_3] = 0.10 - x - 0.10$$

$$x^2/0.10 = 1.77 \times 10^{-5}$$

Thus $x = 1.33 \times 10^{-3} = [OH^-]$

Therefore $[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{(1.33 \times 10^{-3})}$

$$= 7.51 \times 10^{-12}$$

$$pH = -\log(7.5 \times 10^{-12}) = 11.12$$

On addition of 25 mL of 0.1M HCl solution (i.e. 2.5 mmol of HCl) to 50 mL of 0.1M ammonia solution (i.e. 5 mmol of NH_3). 2.5 mmol of ammonia molecules are neutralised. The resulting 75 mL solution contains the remaining unneutralised 2.5 mmol of NH_3 molecules and 2.5 mmol of NH_4^+.

$$NH_3 + HCl \rightarrow NH_4^+ + Cl^-$$

	NH_3	HCl	NH_4^+	Cl^-
	2.5	2.5	0	0
At equilibrium	0	0	2.5	2.5

The resulting 75 mL of solution contains 2.5 mmol of NH4+ ions (i.e. 0.033 M) and 2.5 mmol (i.e. 0.033 M) of uneutralised NH_3 molecules. This NH_3 exists in the following equilibrium:

$$\begin{array}{ccc} NH_4OH & \rightleftharpoons & NH_4^+ + OH^- \\ 0.033M - y & & y \quad\quad y \end{array}$$

where, $y = [OH^-] = [NH_4^+]$

The final 75 mL solution after neutralisation already contains 2.5 m mol NH_4^+ ions (i.e. 0.033M), thus total concentration of NH_4^+ ions is given as:

$$[NH_4^+] = 0.033 + y$$

As y is small, $[NH_4OH] - 0.033$ M and $[NH_4^+] - 0.033$M.

We know, $K_b = \frac{[NH_4^+][OH^-]}{NH_4OH}$

$$= \frac{y(0.033)}{(0.033)} = 1.77 \times 10^{-5}\ M$$

Thus, $y = 1.77 \times 10^{-5} = [OH^-]$

$$[H^+] = 10^{-14} / 1.77 \times 10^{-5} = 0.56 \times 10^{-9}$$

Hence, pH = 9.24.

Hydrolysis of Salts and the pH of their Solution

Hydrolysis is the method in which the reverse reaction of neutralisation occurs.

Salt hydrolysis : salt + water $\rightleftharpoons$ Acid + Base

Hydrolysis of salt of strong acid and weak base

NH_4Cl and NH_4NO_3. are some examples of salt of strong acid and weak base

$$NH_4NO_3 + H_2O \rightleftharpoons NH_4OH + HNO_3$$

$$NH_4^+ + NO_3^- + H_2O \rightleftharpoons NH_4OH + H^+NO_3^-$$

$$NH_4 + H_2O \rightleftharpoons NH_4OH + H^+$$

After this, the solution will be acidic pH < 7.

As there is only the cation of the salt that participates in hydrolysis, therefore it is called cationic hydrolysis.

Hydrolysis of salts of a strong base and weak acid

CH_3COONa and Na_2CO_3 are an example of a strong base and weak acids

$$CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$$

$$CH_3COO^- + Na^+ + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

After this, the solution will be basic pH > 7

As only anionic salt is involved in the hydrolysis process, there it is called anionic hydrolysis.

Hydrolysis of a weak acid and weak base

CH_3COONH_4 and $(NH_4)_2CO_3$ are an example of weak acid and base.

CH_3COONH_4, $(NH_4)_2CO_3$

$$CH_3COONH_4 + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

$$CH_3COO^- + NH_4^+ + H_2O \rightleftharpoons CH_3COOH + NH_4OH$$

The solution pH depends upon the acidic and basic strengths.

Important

➥ *Degree of hydrolysis in such cases is independent of the concentration of solution and pH of such solutions is given by: pH= 7 + 1/2($pK_a - pK_b$)*

Example 4.6: **The pK_a of acetic acid and pK_b ammonium hydroxide are 4.76 and 4.75. Calculate the pH of the ammonium acetate solution. [NCERT]**

Ans. $pH = 7 + \frac{1}{2}[pK_a - pK_b]$

$$= 7 + \frac{1}{2}[4.76 - 4.75]$$

$$= 7 + \frac{1}{2}[0.01] = 7 + 0.005 = 7.005$$

TOPIC 2

BUFFER SOLUTION

The addition of a minimal volume of acid or alkali or dilution in the solution will withstand the change in pH is known as a buffer solution.

Example.

$CH_3COOH + CH_3COONa$. $H_2CO_3 + HCl$

Acidic Buffer

It has acidic pH and is prepared by mixing weak acid and its salt with a strong base. It has a pH below 7. An aqueous solution of an equal to concentration of acetic acid and sodium acetate pH of 4.74.

Preparation of acidic buffer

HA – weak acid

KA – Salt

KOH – Strongbase

$$HA + H_2O \rightleftharpoons H^+ + A^-$$

Acid dissociation constant = $K_a = [H^+][A^-]/HA$

Taking negative log of RHS and LHS:

$-\log K_a = -\log [H^+] - \log[A^-] + \log [A/A]$

$pK_a = pH -$ pH of acid buffer $= pK_a + \log$ ([salt]/acid])

$$pH = pK_a + \log\frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Example. CH_3COOH and CH_3COONa

Basic / Alkaline Buffer

It has acidic pH and is prepared by mixing of a weak base and its salt with strong acid. It has a pH above 7. The aqueous solution of an equal to concentration of ammonium chloride has a pH of 9.25.

Preparation of basic buffer

pOH of basic buffer = $pK_b + \log$ ([salt]/[base])

pH of basic buffer = $pK_a + \log$ ([salt]/[base])

$$pH = pK_a + \log\frac{[\text{Conjugate acid}]}{[\text{Base}]}$$

Example. NH_4Cl and NH_4OH

Salt Buffer

It has neutral pH and is prepared by mixing when a salt solution itself acts as a buffer. It has a pH equal to 7.

Example. $CH_3COONH_4 \rightleftharpoons NH_4^+ + CH_3COO^-$

TOPIC 3

SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

Depending upon the solubility, the salt is categorised into three types:

Category I	Soluble	Solubility > 0.1 M
Category II	Slightly Soluble	0.1M < Solubility < 0.1 M
Category III	Sparingly Soluble	Solubility < 0.01 M

The solubility product constant

It is used for sparingly soluble. Between the substance of ions and unionised solids, there is the involvement of equilibrium.

let us consider an equation.

$$BaSO_4 \underset{\text{in water}}{\overset{\text{saturated solution}}{\rightleftharpoons}} Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)}$$

$$K = K = \frac{[Ba^{2+}][SO_4^{2-}]}{BaSO_4}$$

$$K_{sp} = K\,[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$$

$$K_{sp} = Q_{sp}$$

K_{sp} = solubility product constant or simply solubility product.

A solid salt of the general formula $M_x^{y+}X_y^{x-}$ with molar solubility in equilibrium with its saturated solution.

$$M_xX_{y(s)} \rightleftharpoons xM^{y+}_{(aq)} + yX^{x-}_{(aq)}$$

where $\quad x \times M^{y+} = y \times X^{x-}$

$$K_{sp} = [M^{y+}]^x[X^{x-}]^y = (xS)^x(yS)^y$$

$$= x^x\, y^y\, S^{(x+y)}$$

$$S^{x+y} = K_{sp}/x^x y^y$$

$$S = (K_{sp}/x^x y^y)^{1/x+y}$$

Example 4.7: Calculate the solubility of A_2X_3 pure water, assuming that neither kind of ion react with water. The solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$

Ans. $A_2X_3 \rightarrow 2A^{3+} + 3X^{2-}$

$K_{sp} = [A^{3+}]^2[X^{2-}]^3 = 1.1 \times 10^{-23}$

If $\quad S$ = solubility of A_2X_3

then $\quad [A^{3+}] = 2S;\ [X^{2-}] = 3S$

Therefore, $\quad K_{sp} = (2S)^2(3S)^3 = 108S^5$

Thus, $\quad S^5 = \dfrac{1.1\times10^{-23}}{108}\ 1 \times 10^{-25}$

$S = 1.0 \times 10^{-5}$ mol /L

OBJECTIVE Type Questions

[**1** mark]

Multiple Choice Questions

1. The concentration of the sulphuric acid solution is 0.01M, then calculate its pH.

(a) 4 (b) 3
(c) 1 (d) 2

Ans. *(d) 2*

Explanation: $pH = -\log [H^+]$

$= -\log [10^{-2}] = 2$

Related Theory

- *Negative logarithm of the concentration of hydrogen ion is known as pH.*

Caution

- *It does not have any S.I. unit.*

2. Which of the following is the weak acid–weak base hydrolysis constant?

(a) K_w / K_b (b) K_w / K_a
(c) $K_w / K_a K_b$ (d) $1 / K_a K_b$

Ans. *(c)* $K_w / K_a K_b$

Explanation: $\sqrt{K_w / K_a K_b}$ is the degree of hydrolysis and $\frac{1}{2}K_w + \frac{1}{2}K_a - \frac{1}{2}K_b$ is the pH of the solution.

Related Theory

- *An example is* CH_3COONH_4

3. 40 ml of 0.1 M NH_4OH is mixed with 20 mL of 0.1 M HCL. What is the pH of the mixture? (pK_b of ammonia solution = 4.74)

(a) 4.74 (b) 2.26
(c) 9.26 (d) 5

Ans. *(c) 9.26*

Explanation: 40 mL of 01 M ammonia solution = 40 × 0.1 = 4 milli-equivalent of NH_3 20 mL of 0.1 M HCl = 20 × 0.1 = 2 milli-equivalent HCL

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O$$

Initial milli-eq.	4	2	0
milli-eq. after reaction	4 − 2 = 2	0	2

$$\therefore pOH = pK_b + \log \frac{[NH_4Cl]}{[NH_4OH]} = 4.74 + \log \frac{2}{2}$$

$$= 4.74 + \log 1 = 4.74$$

$$\therefore \quad pH = 14 - 4.74 = 9.26$$

4. K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate is:

(a) 7.005 (b) 4.75
(c) 7.0 (d) Between 6 and 7

[NCERT Exemplar]

Ans. *(c) 7.0*

Explanation: Ammonium acetate is the salt of a weak acid and weak base.

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

$$pH = 7 + \frac{1}{2}(\log(1.8 \times 10^{-5}) - \log(1.8 \times 10^{-5}))$$

$$= 7.0$$

5. The pH of neutral water 25°C is 7.0. As the temperature increases, the ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will the pH of pure water at 60°C?

(a) Equal to 7.0 (b) Greater than 7.0
(c) Less than 7.0 (d) Equal to Zero

[NCERT Exemplar]

Ans. *(c) Less than 7.0*

Explanation: At 25°C, $[H^+] = [OH^-] = 10^{-7}$ and $K_w = [H^+][OH^-] = 10^{-14}$.

On heating, K_w increase. $[H^+][OH^-] > 10^{-14}$ or $[H^+] > 10^{-7}$M or pH < 7.

6. The pH of a 0.005M aqueous solution of sulphuric acid is:

(a) 0.005 (b) 2
(c) 1 (d) 0.01

Ans. *(b) 2*

Explanation: Concentration of protons in sulphuric acid is

$$[H^+] = 0.005 \times 2 = 0.01$$

$$pH = -\log ([H^+]) = -\log (0.01) = 2$$

$$pH = 2$$

7. When equal volumes of 0.1M NaOH and 0.01M HCl are mixed, the pOH of resulting solution is:

(a) 7.0 (b) 1.04
(c) 1.34 (d) 2.0

Ans. *(c) 1.34*

Explanation: $pOH = -\log [OH^-]$

When equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed, as NaOH is more concentrated then

$$OH^- = \frac{0.1 - 0.01}{2} = 0.045M$$

$$pOH = -\log[OH^-]$$

$$= -\log[0.045\ M]$$

$$= 1.34$$

8. What is the molar solubility product for $V_3(PO_4)_5$ in terms of K_{sp}?

(a) $S = (K_{sp} / 84375)^{1/8}$
(b) $S = K_{sp}^{1/8})$
(c) $S = (K_{sp} / 15)^{1/8}$
(d) $S = (K_{sp} / 108)^{1/8}$

Ans. *(a) $S = (K_{sp} / 84375)^{1/8}$*

Explanation: $V_3(PO_4)_5 \rightarrow 3V^{5+} + 5\,PO_4^{3-}$

If S is the solubility of V^{5+} and PO_4^{3-} ions then

$$K_{sp} = [3V^{5+}]^3\,[5PO_4^{3-}]^5$$

$$K_{sp} = [3S]^3\,[5S]^5 = 3^3 \times 5^5 \times S^8$$

$$K_{sp} = 84375 \times S^8$$

$$s = (K_{sp} / 84375)^{1/8}.$$

Assertion-Reason (A-R)

In the following question no. (9-11) a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choice.:

(a) Both (A) and (R) are true and (R) is the correct explanation of (A).
(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).
(c) (A) is true but (R) is false.
(d) (A) is false but (R) is true.

9. **Assertion (A):** A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on the addition of small amounts of acid or alkali.

Reason (R): A solution containing a mixture of acetic acid and sodium acetate acts as a buffer solution around pH of 4.75.

Ans. *(b) Both (A) and (R) are true but (R) is not the correct explanation of (A).*

Explanation: The addition of a minimal volume of acid or alkali or dilution in the solution will withstand the change in pH.

10. Assertion (A): **Neutral solutions always have pH equal to 7.**

Reason (R): **pH of a solution does not depend on temperature.**

Ans. *(d) (A) is false but (R) is true.*

Explanation: At 298 K the pH of neutral solution is 7. as the temperature increase, there will be an increase in the dissociation, thus increases $[H^+]$. Thus, pH of the solution depends upon temperature.

11. Assertion (A): **Aqueous solution of ammonium carbonate is basic.**

Reason (R): **Acidic/basic nature of a salt solution of a salt of a weak acid and weak base depends on Ka and Kb value of the acid and the base forming it.**

[NCERT Exemplar]

Ans. *(a) Both (A) and (R) are true and (R) is the correct explanation of (A).*

Explanation: Both ssertion and reason are true and reason is correct explanation of assertion because K_a and K_b values are responsible for acidic and basic characters of the substances.

CASE BASED Questions (CBQs)

[**4** & **5** marks]

Read the following passages and answer the questions that follow:

12. *The common ion effect helps to finish the particular ion precipitated as sparingly soluble water, with a very low value of solubility product for gravimetric estimation. Thus, we can precipitate silver ion as silver chloride, ferric ion as its hydroxide and barium ion as its sulphate for quantitative estimation. The solubility of a solute in a particular solvent is the maximum concentration that may be achieved under given conditions when the dissolution process is at equilibrium. When a solute's concentration is equal to its solubility, the solution is said to be saturated with that solute. If the solute's concentration is less than its solubility, the solution is said to be unsaturated. A solution that contains a relatively low concentration of solute is called dilute, and one with a relatively high concentration is called concentrated.*

(A) Differentiate the solutions depending upon the solubility of the salt.

(B) Explain the effect of common ions on the solubility of ions salts.

(C) What is buffer capacity?

(D) The molar solubility of $PbBr_2$ is 2.17×10^{-3} M at a certain temperature. Calculate K_{sp} for $PbBr_2$.

Ans. (A) As a general rule for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by the former. Each salt has its characteristics of solubility which depends upon the temperature.

Depending upon the solubility of the salt differentiate into three:

Category I	Soluble	Solubility > 0.1 M
Category II	Slightly Soluble	0.1M < Solubility < 0.01 M
Category III	Sparingly Soluble	Solubility < 0.01 M

(B) (1) One of the ionic concentrations increase then it will combine with the opposite charge ions and certain salt will undergo precipitation till it reaches a point where $K_{sp} = Q_{sp}$

(2) If one of the ionic concentrations is decreasing, then higher will be the salt dissolve which increases both ions concentration till it reaches a point where $K_{sp} = Q_{sp}$ this is used for even the salt like sodium chloride.

(C) The number of millions of acids or bases to be added to a litre of buffer solution to change the pH by one unit is the buffer capacity of the buffer.

Buffer capacity = no. of moles of acid or base per litre/Change in pH

(D) For $PbBr_2$ the expression of solubility product is

$K_{sp} = [Pb^{2+}] [Br^-]^2 = (S)(2S)^2 = 4S^3$

Substitute $S = 2.17 \times 10^{-3}$ in the above expression

Then, $K_{sp} = 4S^3$

$= 4\,(2.17 \times 10^{-3})^3 = 4.1 \times 10^{-8}$

13. *The idea of pH concerns the 'logarithm of the equilibrium' process of water autoionisation. Therefore, the notion is practically limited to aqueous solutions.*

The 'pH of an aqueous solution' is determined using the pH scale, which in water varies typically from 0 to 14. A pH of 7 is neutral. A pH of less than 7 is acidic, while that of 7 or above is considered basic.

A salt is an ionic compound that is formed when an acid and a base neutralize each other. While it may seem that salt solutions are always neutral, they can frequently be either acidic or basic.

Salt hydrolysis is a reaction in which one of the ions from a salt reacts with water, forming either an acidic or basic solution.

Salt formed from:	*Salt Solution*
Strong acid + Strong base	*Neutral*
Strong acid + Weak base	*Acidic*
Weak acid + Strong base	*Basic*

(A) The pK_a of weak acid HA is 4.80 and pK_b of a weak base BOH is 4.78. The pH of an aqueous solutions of corresponding salt BA will be:

(a) 7.01 **(b) 4.79**

(c) 9.22 **(d) 10.0**

[Delhi Gov. QB 2022]

(B) What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH ($K_a = 1.74 \times 10^{-5}$)?

(a) 3.4 **(b) 3.6**

(c) 3.9 **(d) 3.0**

[NCERT Exemplar]

(C) A solution of an acid has a pH = 5.20. Find out the concentration of OH^- ions. ($pK_w = 14$):

(a) 6.58×10^{-9} **(b) 1.58×10^{-9}**

(c) 8.8×10^{-9} **(d) 5.5×10^{-9}**

(D) Which of the following salt gives the highest pH in water?

(a) KCl **(b) NaCl**

(c) Na_2CO_3 **(d) $CuSO_4$** **[Diksha]**

(E) Lemon juice (10 ml) is diluted with an equal amount of water (10 ml). What impact on the pH of the solution is most likely to be seen?

(a) pH of diluted lemon juice would be more than pure lemon juice.

(b) pH of diluted lemon juice would be less than pure lemon juice.

(c) pH of diluted lemon juice would be equal to than pure lemon juice.

(d) No effect on pH.

Ans. (A) *(a) 7.01*

Explanation: For a salt of a weak acid and weak base:

$$pH = \frac{1}{2}\,[pK_w + pK_a - pK_b]$$

$$= \frac{1}{2}(14 + 4.80 - 4.78) = 7.01$$

(B) *(a) 3.4*

Explanation: Given: $C = 0.01\ mol/dm^3$ and $K_a = 1.74 \times 10^{-5}$

So, we have $pH = -\log [H^+]$ and

$$[H^+] = \sqrt{K_a \times C} = \sqrt{1.74 \times 10^{-5} \times 0.01}$$

$$= 4.2 \times 10^{-4}$$

$$pH = -\log (4.2 \times 10^{-4}) = -[\log 4.2 + \log 10^{-4}]$$

$$= 3.4$$

(C) *(b) 1.58×10^{-9}*

Explanation: pH + pOH = pK_w = 14 (given)

$pOH = pK_w - pH = 14 - 5.2 = 8.8$

$[OH^-] = 10^{-pOH} = 10^{-8.8} = 1.58 \times 10^{-9}$

(D) *(c) Na_2CO_3*

Explanation: Salt of weak acid + strong base: pH >7 e.g. Na_2CO_3

Salt of strong acid + weak base : pH < 7 e.g. $CuSO_4$

Salt of strong acid + strong base : pH = 7. e.g. KCl and NaCl

Hence out of the given options, Na_2CO_3 will have the highest pH.

(E) *(a) pH of diluted lemon juice would be more than pure lemon juice.*

Explanation: Therefore, the pH of the solution (diluted lemon juice) would be more than that of pure lemon juice. Lemon juice helps lower the pH levels by raising the number of hydronium ions and decreasing hydroxide ions. As the hydronium ions in the water are what determine the pH level, it is probable that the higher the hydronium content, the higher the pH level.

VERY SHORT ANSWER Type Questions (VSA)

[1 mark]

14. Answer the following:

(A) Conjugate acid or weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?

OH^-, RO^-, CH_3COO^-, Cl^-

[NCERT Exemplar]

(B) Define the buffer.

Ans. (A) $RO^- > OH^- > CH_3COO^- > Cl^-$, this is basic strength order.

(B) The addition of a minimal volume of acid or alkali or dilution in the solution will withstand the change in pH is known as a buffer solution.

15. Explain the following:

(A) In terms of ionisation constant write the expression of difference of relative strength of two weak acids

(B) What is hydrolysis?

Ans. (A) $\dfrac{\text{strength of acid}_1}{\text{strength of acid}_2} = \sqrt{\dfrac{K_{a_1}}{K_{a_2}}}$

(B) Hydrolysis is the method in which reverse reaction of neutralisation occurs.

16. What will be the pH of a 10^{-10}M NaOH solution?

Ans. At 25°C, concentration of OH^- ions is 10^{-7} NaOH as present in water.

But the concentration in this case, is given as of $[OH^-] = (10^{-7} + 10^{-10})$ M = 1.001×10^{-7}.

Now,

$$pOH = \log [OH^-] = -\log (1.001 \times 10^{-7})$$
$$= 7 - \log (1.001) = 7 - 0.00043 = 6.99$$
$$pH = 14 - pOH = 14 - 6.99 = 7.01$$

17. The solubility of silver sulphate in the water at 100°C is approximately 1.4 g per 100 mL. What is the solubility product of this salt at 100°C?

Ans. The molecular weight of Ag_2SO_4 is 312g/mol, is

$$\text{Solubility,} \quad S = \frac{1.4 \text{ g}}{0.1 \text{ L}} = 14 \text{ g/L}$$

$$\text{Molarity} = \frac{14}{312} \text{ M} = 0.04487\text{M}$$

The expression for the solubility product is:

$$K_{sp} = [Ag^+]^2[SO_4^{2-}] = (2S)^2 (S) = 4S^3$$

Substitute S = 0.04487 M in the above expression.

$$K_{sp} = 4S^3 = 4 (0.04487)^3 = 3.6 \times 10^{-4}$$

SHORT ANSWER Type-I Questions (SA-I)

[2 marks]

18. Based on the equation pH = – log[H⁺], the pH of 10^{-8} mol dm^{-3} a solution HCl should be 8. However, it is observed to be less than 7.0. Explain the reason. [NCERT Exemplar]

Ans. According to the facts, it tells us that the solution is very dilute and production of hydronium ions by reacting HCl with H_2O. Therefore, greater the (H^+) concentration leads to a decline in the pH. Hence, we cannot disregard the H_3O^+ ions concentration in the solution.

Thus, the overall pH will be $[H_3O^+] = 10^{-8} + 10^{-7}$ M ≈ 7. So, it will be the acidic solution.

19. Arrange the following in increasing order of pH.

KNO_3 CH_3COONa NH_4Cl $C_6H_5COONH_4$

Ans. KNO_3 (salt of strong acid-strongbase), solution is neutral, pH = 7.

CH_3COONa (salt of weak acid-strong base), solution is basic, pH > 7.

NH_4Cl (salt of strong acid-weak base), solution is acidic, pH < 7.

$C_6H_5COONH_4$ (both weak but NH_4OH is slightly stronger than C_6H_5COOH. pH is close to 7 but slightly >7.

$NH_4Cl < C_6H_5COONH_4 < KNO_3 < CH_3COONa$.

20. Find the molar solubility of $PbCl_2$ in 0.20M $Pb(NO_3)_2$ solution (K_{sp} for $PbCl_2 = 1.6 \times 10^{-5}$).

Ans.

$$[Pb^{2+}] = [Pb(NO_3)_2] = 0.20M$$

The expression for the solubility product is

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

Substitute values in the expression for the solubility product.

$$K_{sp} = [Pb^{2+}] \times [Cl^-]^2$$

$$1.6 \times 10^{-5} = 0.20 \times [Cl^-]^2$$

$$[Cl^-]^2 = 8 \times 10^{-5}$$

$$[Cl^-] = 8 \times 10^{-3}M$$

The molar solubility of $PbCl_2$ in 0.20M $Pb(NO_3)_2$ is

$$= \frac{[Cl^-]}{2} = \frac{8.9 \times 10^{-3}M}{2} = 4.6 \times 10^{-3}M$$

21. A solution of 0.1M NH_3 ($K_b = 1.8 \times 10^{-5}$). Calculate the pH value.

Ans. $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4]}$$

$$[NH_4^+] = [OH^-]$$

$$K_b = \frac{[OH^-]^2}{[NH_4^+]}$$

$$[OH^-] = \sqrt{K_b \times [NH_3]} = \sqrt{1.8 \times 10^{-5} \times 0.1}$$

$$= \sqrt{1.8 \times 10^{-3}} = 1.34 \times 10^{-3}$$

$$[NH_4^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.34 \times 10^{-3}}$$

$$= 7.46 \times 10^{-12}$$

$$pH = -\log [NH_4^+]$$
$$= -\log (7.46 \times 10^{-12})$$
$$= -(-12 - \log 7.46)$$
$$= 12 - 0.88 = 11.12$$

⚠ **Caution**

➥ *K_b does not have any dimension.*

22. $\frac{N}{1000}$ the sodium hydroxide solution is supposed to be fully ionised. Then calculate the pH.

Ans.

$$[NaOH] = [OH] = 10^{-3}N = 10^{-3}M$$

$$\text{Given } [H_3O^+][OH^-] = K_w = 10^{-14}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-3}} = 10^{-11}$$

$$pH = -\log[H_3O^+] = -\log 10^{-11} = 11$$

SHORT ANSWER Type-II Questions (SA-II)

[3 marks]

23. Answer the following:

(A) Write the pH value for the following substances.

(i) Black coffee (ii) Milk
(iii) Human blood (iv) Human saliva
(v) Egg white (vi) Lime water

(B) Write the uses of buffer solution and what will happen in the absence of buffer in enzyme action?

Ans. (A) (i) 5.0– the caffeine is slightly alkaline in nature.

(ii) 6.8– due the presence of lactic acid.

(iii) 7.8– due to the presence of bicarbonate unit.

(iv) 6.4– bacteria present in the mouth break down the carbohydrates and lead to formation of lactic acid, butyric acid, aspartic acid.

(v) 7.8– it is naturally alkaline

(vi) 10.5– lime water is a saturated solution of a base called calcium hydroxide in water.

(B) (1) In the pH regulation is the use of bacarbonate and carbonic acid buffer system in order to regulate the pH of blood.

(2) It also maintains an optimum pH for enzyme activity in mainly organisms.

The absence of these buffers leads to the slowing of the enzyme action, loss in enzyme properties or even denatured of the enzymes. This denaturation process can even permanently deactivate the catalytic action of the enzymes.

24. Explain the following question:

(A) The factors affecting the acidic strength.

(B) The relation between K_a and K_b

Ans. (A) (1) The decreasing order of H–A bond

$$\xrightarrow{\text{Size increases}}$$

$$HF << HCl << HBr << HI$$

$$\xrightarrow[\text{Acid strength increases}]{}$$

The *H–A* bond will be stronger acid when the energy needed to spilt the bond is less. As we go down to the group the size of the more. Thus, decrease in the strength of *H–A* bond. Therefore, the strength of the acid is greater.

(2) The electronegativity A is higher, then the acid strength will be more in a period.

$$\xrightarrow{\text{Electronegativity of A increases}}$$

$$CH_4 < NH_3 < H_2O < HF$$

$$\xrightarrow[\text{Acid strength increases}]{}$$

(B) For the net reaction we get an equilibrium constant by adding two or more than two reactions which will be similar to the equilibrium constant product for the independent reaction.

$$K_{net} = K_1 \times K_2 \times \_\_\_\_\_$$

In the pair of conjugate acid-base

$$K_a \times K_b = K_w$$

In $$B_{(aq)} = H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

$$K_b = [BH^+]\,[OH^-]/[B]$$

As the concentration of water remains constant it has been omitted from the denominator and incorporated within the dissociation constant. Then multiply and divided the above expression by $[H^+]$, then

$$K_b = [BH^+]\,[OH^-]\,[H^+]\,/\,[B]\,[H^+]$$

$$= \{[OH^-]\,[H^+]\}\,\{[BH^+]\,/\,[B]\,[H^+]\}$$

$$= K_w / K_a$$

$$= K_a \times K_b = K_w$$

If we take negative logarithm of both sides of the equation, then pK values of the conjugate acid and base are related to each other by the equation:

$$pK_a + pK_b = pK_w = 14 \text{ (at 298K)}$$

25. **The values of Ksp of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6.0×10^{-17} respectively. Which salt is more soluble. Explain.**

Ans.

$$AgCN \rightleftharpoons Ag^+ + CN^-$$

$$K_{sp} = [Ag^+][CN^-] = 6 \times 10^{-17} \quad \text{...(i)}$$

Let $[Ag^+] = S$, then $[CN^-] = S$

$\therefore$ From eq. (i) $S \times S = 6 \times 10^{-17}$

Then, $S = \sqrt{6 \times 10^{-17}} = 7.8 \times 10^{-9}$

$$Ni(OH)_2 \rightleftharpoons Ni^{+2} + 2OH^- \quad \text{...(ii)}$$

$$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$$

Let $[Ni^{2+}] = S'$, then $[OH^-] = 2S'$

From equation (ii):

$$(S') \times (2S')^2 = 2 \times 10^{-15}$$

$$4(S')^3 = 2 \times 10^{-15}$$

$$(S')^3 = 2 \times 10^{-15}/4 = 0.5 \times 10^{-15}$$

or $S' = 0.58 \times 10^{-4}$

Since solubility of $Ni(OH)_2$ is more than AgCN, so, $Ni(OH)_2$ is more soluble than AgCN.

26. **Find the pH of 0.05 M NH_4Cl (ammonium chloride), using the value $K_b(NH_3) = 1.8 \times 10^{-5}$ mol L^{-1}**

Ans.

$$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)}$$

$$= \frac{1.00 \times 10^{-14} \text{ mol}^2 L^{-2}}{1.8 \times 10^{-5} \text{ mol } L^{-1}}$$

$$= 5.56 \times 10^{-10} \text{ mol } L^{-1}$$

We can now evaluate the hydronium-ion concentration with the usual approximation:

$$[H_3O^+] = \sqrt{K_a C}$$

$$= \sqrt{5.56 \times 10^{-10} \text{ mol } L^{-1} \times 0.05 \text{ mol } L^{-1}}$$

$$= 5.27 \times 10^{-6} \text{ mol } L^{-1}$$

Hence pH $= -\log(5.27 \times 10^{-6}) = 5.28$

LONG ANSWER Type Questions (LA)

[**4** & **5** marks]

27. **A sparingly soluble salt gets precipitated only when the product of the concentration of its ions in the solution (Q_{sp}) becomes greater than its solubility product. If the solubility**

of $BaSO_4$ in water is 8×10^{-4} mol dm^{-3}, calculate its solubility in 0.01 mol dm^{-3} of H_2SO_4. [NCERT Exemplar]

Ans.

	$BaSO_4 \rightleftharpoons$	Ba^{2+} +	SO_4^{2-}
	1	0	0
At t = 0	1-S	S	S
At equilibrium	1-S	S	(S+0.01)

K_{sp} for $BaSO_4$ in water $= [Ba^{2+}][SO_4^{2-}]$

$$= S \times S = S^2$$

$$K_{sp} = (8 \times 10^{-4})^2$$

$$= 64 \times 10^{-8}$$

In presence of H_2SO_4

$$K_{sp} = (S)(S + 0.01)$$

K_{sp} being constant

$$(S)(S + 0.01) = 64 \times 10^{-8}$$

$$S^2 + 0.01S = 64 \times 10^{-8}$$

$$S^2 + 0.01S - 64 \times 10^{-8} = 0$$

$$S = \frac{-0.01 \pm \sqrt{(0.01)^2 + (4 \times 64 \times 10^{-8})}}{2}$$

$$= \frac{-0.01 \pm \sqrt{10^{-4} + (256 \times 10^{-8})}}{2}$$

$$= \frac{-10^{-2} + (1.012 \times 10^{-2})}{2} = \frac{(-1 + 1.012) \times 10^{-2}}{2}$$

$$= 6 \times 10^{-4} \text{ mol dm}^{-3}$$

28. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having pH = 6 and pH = 4 respectively. [NCERT Exemplar]

Ans. pH of solution A = 6

Therefore, concentration of $[H^+] = 10^{-6}$ molL^{-1}

pH of solution B = 4

Therefore, concentration of $[H^+] = 10^{-4}$ molL^{-1}

On mixing 1L each solution, then total volume = 1L + 1L = 2L

Total amount of H^+ in 2L solution formed by mixing solution A and B $= 10^{-6} + 10^{-4}$ mol

This amount is present in 2L solution

$$\text{Total } [H^+] = \frac{10^{-4}(1 + 0.01)}{2} = \frac{1.01 \times 10^{-4}}{2} \text{ mol L}^{-1}$$

$$= \frac{1.01 \times 10^{-4}}{2} \text{ mol L}^{-1}$$

$$= 0.05 \times 10^{-4} \text{ mol L}^{-1}$$

$$= 5 \times 10^{-6} \text{ mol L}^{-1}$$

$$pH = -\log [H^+] = -\log (5 \times 10^{-5})$$

$$= -[\log 5 + (-5 \log 10)]$$

$$= -\log 5 + 5$$

$$= 5 - \log 5$$

$$= 5 - 0.6990$$

$$= 4.3010 = 4.3$$

◆