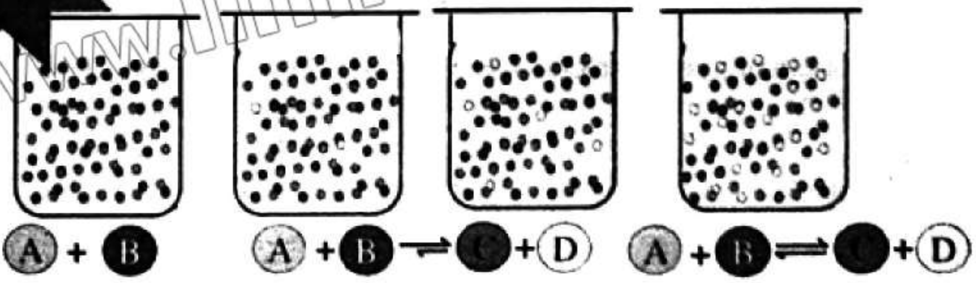
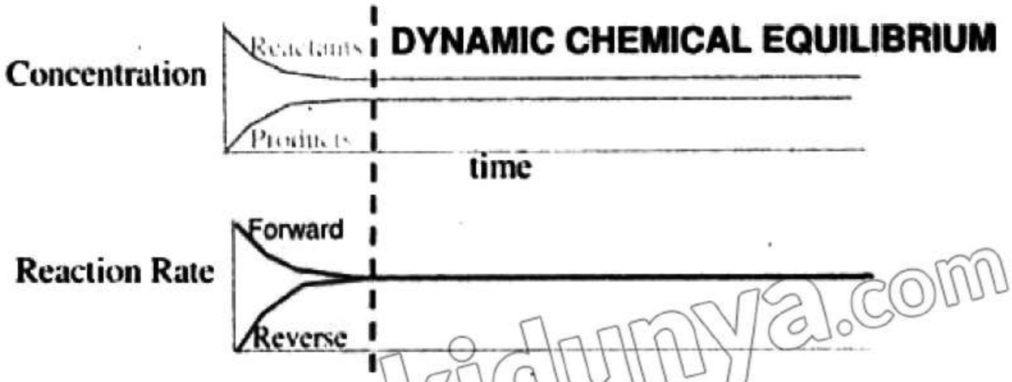
UNIT 03





CHEMICAL EQUILIBRIA

Student Learning Outcomes (SLOs)

- Explain common ion effects giving suitable examples.
- Use the extent of ionization and the acid dissociation constant, K_a, to distinguish between strong and weak acids.
- Use the extent of ionization and the base dissociation constant, K_b, to distinguish between strong and weak bases.
- Explain what is meant by a chemical buffer and how a buffer system works. (For context this should include: a. defining what is a buffer solution. b. Explain how a buffer solution can be made. c. explaining how buffer solutions control pH: use chemical equations in these explanations. d. Describe and explain the uses of buffer solutions, including the role of HCO_3^- in controlling pH in blood.
- Calculate concentration of slightly soluble salts.
- State what is meant by the term partition coefficient, K_{pc}.
- Calculate a partition coefficient for a system in which the solute is in the same physical state in the two solvents.
- Explain the factors affecting the value of a partition coefficient in terms of the polarities of the solute and the solvent used.

How do substances behave in various environments? This requires an understanding of chemical reactions and equilibrium. When an additional ion is added, the common ion effect predicts solution reactions. The strength of acids and bases can be estimated from their dissociation constants, which differentiate strong acids from weak ones. Buffer solutions maintain pH equilibrium and regulate blood pH. This you will understand in this chapter. The distribution of solutes among solvents is predicted by the partition coefficient, which is useful in estimating the distribution of drugs within the body. So it is very important for drug design. These concepts play a key role in industrial and environmental science

3.1 Strength of Acids and Bases

The degree to which different Bronsted acids give off protons is called "acid strength". A relatively strong acid is an acid that can give off more protons than another acid. Hydrochloric acid, for example, is relatively strong compared to acetic acid, which is relatively strong relative to water. Bases differ in the degree to which they accept protons as well. A strong base can accept protons to a greater extent than another base, so ammonia is relatively stronger relative to water because it can accept protons to a higher degree than water.

3.1.1 Strong and Weak Acids

The extent of ionization and the acid dissociation constant K_a can be used to distinguish between strong and weak acids.

The strength of an acid is generally expressed in terms of the acid ionization constant, K_a of the acid. Consider the case of ionization of a general acid HX in water. In this aqueous solution, the established equilibrium may be represented as follows:

$$HX + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + X^-_{(aq)}$$

The equilibrium constant K for this ionization process may be written as follows:

$$K = \frac{[H_3O^+][X^-]}{[HX][H_2O]}$$

or $$K[H_2O] = \frac{[H_3O^+][X^-]}{[HX]}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, $K[H_2O]$ is another constant and is designated as K_a.

$$K[H_2O] = K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state. It must be kept in mind that the acid dissociation constant, K_a, is dependent on temperature. Therefore, the value of K_a should be mentioned along with the temperature at which K_a was determined. The dissociation constant, K_a, of acetic acid in water at 25°C is 1.8×10^{-5}. The comparison of K_a Values of different acids provides a method to compare their strengths.

"The greater the value of K_a, the stronger the acid".

The values of K_a are usually inconvenient numbers, therefore, for convenience, these values are converted to pK_a values. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Since pK_a refers to the negative logarithm of K_a, the lower the pK_a value, the stronger the acid, since a lower pK_a value corresponds to a higher K_a value. Table 3.1 lists the ionization constants and pK_a values of some common acids in water at 25°C. Which acid is the strongest? Which acid is the weakest?

Table 3.1: Ionisation constants and pK_a of Acids

Name of Acid	Formula	K_a	pK_a
Perchloric acid	$HClO_4$	1.0×10^{10}	-10.0
Hydroiodic acid	HI	1.0×10^{10}	-10.0
Hydrobromic acid	HBr	1.0×10^{9}	-9.0
Hydrochloric acid	HCl	1.0×10^{6}	-6.0
Sulphuric acid	H_2SO_4	1.0×10^{3}	-3.0
Hydrofluoric acid	HF	7.2×10^{-4}	+3.1
Formic acid	$HCOOH$	1.8×10^{-4}	+3.75
Benzoic acid	C_6H_5COOH	6.3×10^{-5}	+4.2
Acetic acid	CH_3COOH	1.8×10^{-5}	+4.7
Phenol	C_6H_5OH	1.3×10^{-10}	+8.9
Water	H_2O	1.8×10^{-16}	+15.7

Which acid is stronger HCl or HF?

Example 3.1

Calculate the concentration of H^+ ions of a solution that contains

1.0M HF ($K_a = 7.2 \times 10^{-4}$)

Solution:

$$HF_{(aq)} \rightleftharpoons H^+_{(aq)} + F^-_{(aq)}$$

	$HF_{(aq)}$	$H^+_{(aq)}$	$F^-_{(aq)}$
Initial conc.	1.0M	0	0
Eq. conc. (mole dm^{-3})	$1.0-x$	x	x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$7.2\times10^{-4} = \frac{x \cdot x}{1.0 - x}$$

Since x is very small as compared to 1.0, the term in the denominator can be approximated as follows:

$$1.0 - x = 1.0$$

$$7.2\times10^{-4} = \frac{x^2}{1}$$

$$x = 0.268M$$

$$[H^+] = 0.268M$$

3.1.2 Strong and Weak Bases

The strength of a base is the ability to accept a proton from a solvent. Hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide are strong bases and ionize completely in aqueous solution.

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

The OH^- ion thus formed is a Bronsted base because it can accept proton H^+.

$$OH^- + H^+ \longrightarrow H_2O$$

The ability of a base to accept a proton from an acid, usually water, is termed as the strength of the base. For a base B, an equilibrium reaction with water can be represented by the following equation:

$$B + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

The equilibrium constant K_b is called the base ionization constant and can be derived. As;

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

K_b value will be large if the degree of ionization of the base B is high i.e. if the base B is strong. The Value of K_b will be small for a weak base B. Again, for convenience, a parameter pK_b has been devised to express the K_b value in convenient numbers. Thus, pK_b is defined as the negative logarithm of K_b.

$$pK_b = -\log K_b$$

Table 3.2: K_b and pK_b Values of Some Common Bases

Name of Base	Formula	K_b	pK_b
Diethlyamine	$(C_2H_5)_2NH$	9.6×10^{-4}	3.02
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}	3.25
Methylamine	$CH_3\,NH_2$	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	C_5H_5N	5.6×10^{-9}	8.25
Aniline	$C_6H_5\,NH_2$	4.3×10^{-10}	9.37

According to these values, ammonia is a stronger base than pyridine and aniline but weaker than methylamine and ethylamine. Also, diethyl amine is the strongest base among all those listed in Table 3.2.

3.2 Buffer Solutions and their Applications

A buffer solution is a solution, the pH of which does not change significantly when a small amount of acid or base is added to it. Such a solution has a constant pH which does not change keeping it constant for a long time.

Types of buffer solutions

A buffer solution can be made in two ways:

(1) By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. e.g. $CH_3COOH + CH_3COONa$.

(2) By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with a pH of more than 7. e.g. $NH_4OH + NH_4Cl$.

Buffer Action:

Consider a buffer solution of CH_3COOH and CH_3COONa. The common ion effect helps us to understand how the buffer will work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa, a strong electrolyte is added to the CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to the common ion effect of CH_3COO^-.

$$CH_3COOH_{(l)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$CH_3COONa_{(s)} \rightleftharpoons CH_3COO^-_{(aq)} + Na^+_{(aq)}$$

(i) Suppose we add a few drops of HCl to it. Its H^+ ions are used up by CH_3COO^- ions.

Thus the addition of HCl will not change the pH of the buffer solution.

$$CH_3COOH_{(l)} \underset{}{\overset{H_2O}{\rightleftharpoons}} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \rightleftharpoons CH_3COOH_{(aq)}$$

(ii) In the same buffer solution, if a strong base is added, it is neutralised by the acid.

$$CH_3COOH_{(l)} \overset{H_2O}{\rightleftharpoons} CH_3COO^-_{(aq)} + H^+_{(aq)}$$

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$H^+_{(aq)} + OH^-_{(aq)} \rightleftharpoons H_2O_{(l)}$$

Thus the addition of NaOH will not change the value of pH.

3.2.1 Calculation of pH of Buffer Solution

The concentration of conjugate base in the reaction mixture is predominately supplied by the salt which is a strong electrolyte. Therefore, assuming the concentration of conjugate base is equal to that of salt and the original concentration of acid as equilibrium concentrations, the pH of a buffer can be calculated.

The following example explains the calculations associated with buffer solutions.

Example 3.2

(a) Calculate the pH of an acetic acid-sodium acetate buffer solution containing 1.0 moles of each component.

(b) What will be the pH of this solution after the addition of 0.01 mole of hydrochloric acid to 1dm^3 of the solution? Assume that the volume of the solution remains unchanged with the addition of hydrochloric acid. (K_a for acetic acid is 1.8×10^{-5}).

Solution

(a) The pH of the buffer solutions can be calculated by assuming the equilibrium concentration of both the acid and its conjugate base as the starting concentration.

Thus $[CH_3CO_2H] = 1.0M$ $[CH_3COO^-] = 1.0M$

For acetic acid dissociation;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} = \frac{[1.0][H^+]}{[1.0]}$$

Thus, the pH of the buffer solution is 4.745.

(b) After HCl addition:

$$HCl_{(aq)} \longrightarrow H^{+}_{(aq)} + Cl^{-1}_{(aq)}$$

0.01 mole 0.01 mole 0.01 mole

Initially, there were 1.0 mole of CH_3COOH and 1.0 mole of CH_3COO^- present per dm^3 of the solution. After the addition of hydrochloric acid 0.01 mole of CH_3COO^- ions is combined with the H^+ ions formed from the dissociation of 0.01 mole of added hydrochloric acid. This can be written as:

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3CO_2H_{(aq)}$$

0.01 mole 0.01 mole 0.01 mole

Thus, the numbers of moles of acetic acid and acetate ions, after the addition of hydrochloric acid are:

$$CH_3CO_2H = (1.0+0.01)\text{ mole} = 1.01\text{mole}$$

$$CH_3COO^- = (1.0-0.01)\text{ mole} = 0.99\text{mole}$$

The equilibrium equation for this new situation can be written as;

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3CO_2H]}$$

or

$$[H^+] = \frac{Ka[CH_3CO_2H]}{[CH_3.COO^-]}$$

$$[H^+] = \frac{1.8\times10^{-5}(1.01)}{0.99}$$

$$pH = -\log(1.83\times10^{-5})$$

$$= 4.736$$

Notice there is a slight change in pH from 4.745 to 4.736 which is only a difference of 0.009. Thus, a buffer does a very good job in limiting the change in pH to a very small amount.

3.2.2 Applications of Buffer Solutions

Buffers play a crucial role in various everyday applications, helping to maintain stability and prevent abrupt changes in different systems. Here are some important applications of buffers in everyday life.

1. The buffer system in blood plasma

The bicarbonate ion (HCO_3^-) plays a crucial role in maintaining blood pH through the bicarbonate buffer system. Blood pH is a measure of its acidity or alkalinity, and it must be tightly regulated for various physiological processes to function properly. The normal pH range of blood is approximately 7.35 –7.45, a value higher than 7.8 or lower than 6.8 can lead to death.

In the bicarbonate buffer system, there is a reversible exchange of carbon dioxide (CO_2) and bicarbonate ions in the blood. The reaction can be summarized as follows:

(a) Formation of carbonic acid (H_2CO_3):

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

(b) Decomposition of carbonic acid into bicarbonate (HCO_3^-) and hydrogen ion (H^+):

$$H_2CO_{3(aq)} \qquad HCO^-_{3(aq)} + H^+_{(aq)}$$

This system is catalyzed by an enzyme found in red blood cells called carbonic anhydrase. CO_2, H_2CO_3, HCO_3^- and H^+ levels are related, and any imbalance can affect the pH of the blood. Thus HCO_3^- helps regulate blood pH:

Neutralization of acids:

When there are many acids (H^+ ions) in the blood, bicarbonate acts as a base, binding to these hydrogen ions and forming carbonic acid. This reaction helps to neutralize and eliminate excess acidity:

$$HCO^-_{3(aq)} + H^+_{(aq)} \rightleftharpoons H_2CO_{3(aq)}$$

Neutralization of bases:

Conversely, if there are many bases in the blood, such as hydroxide ions (OH^-), the carbonic acid dissociates, releasing hydrogen ions that can combine with excess bases:

$$OH^-_{(aq)} + H_2CO_{3(aq)} \rightleftharpoons HCO^-_{3(aq)} + H_2O_{(l)}$$

Participating in these reversible reactions, bicarbonate ions help maintain the acid-base balance in the blood. This buffer system is crucial in preventing rapid changes in blood pH and provides a stable environment for enzymes and other biochemical processes to function optimally. The respiratory and renal systems also play an important role in regulating CO_2 and bicarbonate levels to maintain blood pH in a normal range.

2. Household Cleaning Products:

Detergents: Many cleaning agents and detergents contain buffers to maintain a stable pH, ensuring effective cleaning without causing harm to the surface or skin.

3. Personal Care Products:

Shampoos and Soaps: Buffers are often used to maintain the pH of shampoos and soaps, preventing skin irritation and ensuring the products are gentle.

4. Swimming Pools:

Water Treatment: Buffers are employed in swimming pools to help maintain a stable pH level, preventing corrosion of pool equipment and ensuring a comfortable environment for swimmers.

5. Food and Beverage Industry:

Food Preservation: Buffers are used in food processing to control acidity, preserve flavours, and maintain the stability of certain food products.

Beverage Production: Buffers help control the pH in beverages, ensuring consistency in taste and preventing spoilage.

6. Photography:

Developer Solutions: Buffers are used in photographic developer solutions to maintain a stable pH, allowing for controlled and consistent film or print development.

3.3 Solubility Product and Precipitation Reactions

Now we will discuss some of the important equilibria which have some analytical importance.

3.3.1 Solubility Product

When an excess of slightly soluble ionic compound is mixed with water. Some of it dissolves and the remaining compound settles at the bottom. Dynamic equilibrium is established between an undissolved solid compound and its ions in the saturated solution. For example, when CaF_2 is mixed with water. The following equilibrium is established.

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

K_c for this equilibrium can be written as

$$K_c = \frac{[Ca^{+2}][F^-]^2}{[CaF_2]}$$

DO YOU KNOW

K_{sp} is used for solutes which are only slightly soluble and do not completely dissolve in solution. The higher the K_{sp} value of a compound, the more it is soluble in water.

Since CaF_2 is a slightly soluble salt its concentration almost remains constant.

Therefore,

$$K_c[CaF_2] = [Ca^{+2}][F^-]^2$$

$$K_{sp} = [Ca^{+2}][F^-]^2$$

Where K_{sp} is a constant known as **the solubility product constant. It is defined as the product of the molar concentrations of ions, each raised to a power which is equal to the coefficient of the ion in the balanced chemical equation.**

In general, K_{sp} expression of any slightly soluble ionic compound, A_mB_n can be written as

$$A_mB_{n(s)} \rightleftharpoons mA^{+n}{}_{(aq)} + nB^{-m}{}_{(aq)}$$

$$K_{SP} = [A^{+n}]^m [B^{-m}]^n$$

This means that the solubility product constant is equal to the product of the equilibrium concentration of ions each raised to a power equal to the number of such ions in the formula unit of the compound.

CONCEPT ASSESSMENT EXERCISE 3.1

Write the dissociation reaction and the solubility product constant expression for each of the following solids.

1. $PbSO_4$
2. $Al(OH)_3$
3. $BaSO_4$

3.3.2 Calculating Concentrations of ions

Given the K_{sp} for AgBr ($K_{sp} = 1.60\times10^{-10}$), we can use the K_{sp} expression to calculate the concentrations of each ion in the solution.

If we represent the x moles of AgBr dissolved in one dm^3 of water

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)}$$

$$x \qquad\qquad x \qquad\qquad x$$

$$K_{sp} = [Ag+][Br-]$$

$$1.60\times10^{-10} = x.x$$

$$X^2 = 1.6\times10^{-10}$$

$$X = 1.26 \times 10^{-5}M$$

$$\text{So, } [Ag^+] = [Br^-] = 1.26 \times 10^{-5}M$$

Slightly soluble salts dissociate only to a small extent in water, leading to low ion concentrations. To calculate the concentration of these salts in solution, we use their solubility product constant (K_{sp}).

The K_{sp} expression relates the concentrations of the ions in equilibrium with the undissolved salt.

Steps to calculate the concentration:

1. Write the dissociation equation for the salt.
2. Set up the K_{sp} expression.
3. Solve for ion concentrations based on stoichiometry.

Example 3.3

Calculate the concentration of Silver chloride (AgCl) in its aqueous solution.

1. **Dissociation:**

   $AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$

2. **Ksp expression:**

   $K_{sp} = [Ag^+][Cl^-]$

   For AgCl, $K_{sp} = 1.8\times10^{-10}$ at 25°C.

3. **Concentration Calculation:**

   Since each mole of AgCl gives one mole of Ag^+ and Cl^- ions, let the solubility of AgCl be x mol/dm³. Then,

   $$Ksp = [x][x]$$
   $$1.8\times10^{-10} = x^2$$
   $$x^2 = 1.8 \times 10^{-10}$$
   $$x = 1.34\times10^{-5}\ mol/dm^3$$

   Thus, the solubility (or concentration of Ag^+ and Cl^-) in water is approximately 1.34×10^{-5} mol/dm³

CONCEPT ASSESSMENT EXERCISE 3.2

1. K_{sp} for PbF_2 is 4×10^{-8}. Calculate the concentration Pb^{2+} and F^- ions in solution.

   Ans : 2.5×10^{-3} mol dm^{-3}, 4.3×10^{-3} mol dm^{-3}

2. K_{sp} for $BaSO_4$ is 1×10^{-10}. Write the equation and the equilibrium expression for the dissolving of barium sulphate. Also calculate the concentration of each ion.

   Ans: 1×10^{-5} mol dm^{-3} each.

3.4 Common Ion Effect

An interesting situation arises when a weak electrolyte and a salt containing a common ion are present simultaneously in an aqueous solution. For example, in a solution of weak acid, hydrofluoric acid $K_a = 7.2 \times 10^{-4}$, its salt sodium fluoride produces the common ion.

$$HF_{(aq)} \xrightleftharpoons{H_2O} H^+_{(aq)} + F^-_{(aq)}$$

$$NaF_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + F^-_{(aq)}$$

Since HF is a weak electrolyte, it slightly dissociates. NaF being a strong electrolyte breaks up completely into its ions. The common ion F^- produced by NaF will upset its equilibrium. This will increase the concentration of F^- ions. According, to Le Chatelier's principle, the equilibrium will shift to the left to use some of the F^- ions. This will decrease the dissociation of HF. Thus dissociation of HF will decrease in the presence of dissolved NaF. This means as a result of the equilibrium shift, the concentration of HF will increase.

Similarly, when a highly soluble salt is added to the saturated solution of a less soluble salt containing a common ion. *The degree of dissociation* of the less soluble salt decreases. Therefore, it causes a decrease in its solubility.

DO YOU KNOW

The separation and identification of cations into analytical groups is based on solubility product principle and common ion effect. In general, any procedure that involves precipitation follows these principles.

The term common ion effect is used to describe the behaviour of a solution in which the same ion is produced by two different compounds. **"The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of highly soluble electrolyte containing a common ion is called common ion effect".**

Examples

i. Potassium per chlorate $KClO_4$ is moderately soluble in water. When highly soluble KCl is added to the saturated solution of $KClO_4$. It causes an increase in the concentration of K^+ ion.

$$KClO_{4(s)} \rightleftharpoons K^+_{(aq)} + ClO^-_{4(aq)}$$

$$KCl_{(s)} \longrightarrow K^+_{(aq)}\ Cl^-_{(aq)}$$

According to Le Chatelier's principle K^+ ions will react with ClO_4 ions to form $KClO_{4(s)}$ This will suppress, the ionization of $KClO_4$. Thus it will precipitate out.

ii. When HCl gas is passed through the saturated solution of NaCl (Brine), it increases the concentration of Cl^- ion.

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl^{-1}_{(aq)}$$

According to Le Chatelier's principle Cl^- ions will combine with Na^+ ions to form precipitate of a pure NaCl.

Self Check Exercise 3.3

i. Ammonium Chloride, NH_4Cl is a water-soluble salt. What will happen if this salt is added to a solution containing ammonium hydroxide?

$$NH_4OH_{(aq)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

ii. Carbonic acid is a weak acid. It ionizes in water as follows

$$H_2CO_{3(aq)} \rightleftharpoons 2H^+_{(aq)} + CO^{-2}_{3(aq)}$$

What will happen if a strong electrolyte such as Na_2CO_3 is added to a solution containing carbonic acid?

3.5 The Partition Coefficient

If you put two immiscible liquids like ether and water in a separatory funnel and shake. On standing, you can see two layers. Ether is less dense, so it forms the upper layer. Assume that solute X dissolves in both liquids. If you prepare a solution of known concentration of X in water and mix it with ether in a separatory funnel and shake well. On standing, the two layers separate again. Now determine the concentration of the water layer. You will notice a decrease in concentration. Why? Where did the solute go? Analysis of the ether layer shows that there is also a solute in the ether layer. This means that the solute is distributed between the two solvents. A dynamic equilibrium is created between these two solutions. At equilibrium, the concentration of X becomes constant in both layers.

$$\text{X(in water)} \rightleftharpoons \text{X(in ether)}$$

$$K_{PC} = \frac{[\text{X in ether}]}{[\text{X in water}]}$$

This equilibrium constant is called the partition coefficient and is represented by the symbol K_{pc}. It has a constant value at a constant temperature.

The distribution law, or Nernst distribution law, gives a generalization that governs the distribution of a solute between two immiscible solvents. This law was first given by Nernst, who studied the partitioning of several solutes between various suitable pairs of solvents.

The partition coefficient (K_{pc}) is defined as the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature. The partition coefficient is a ratio of two concentrations, so it has no units.

3.5.1 Calculation of Partition Coefficient

The **partition coefficient** (K_{pc}) for a system in which the solute is in the same physical state in the two solvents can be calculated using the equilibrium expression.

ACTIVITY 3.1: Calculating the partition coefficient

Procedure

- Measure 100 cm^3 of a 0.150M solution of aqueous methylamine and add it into a separatory funnel.
- Add 75 cm^3 of an organic solvent in the separatory funnel.
- Shake the separatory funnel gently but thoroughly to allow the solute to distribute between the two solvents. Allow the system to reach equilibrium (about 5-10 minutes).
- Let the layers settle and separate the two solvents into different beakers.
- Measure the concentration of the solute in each solvent.

Calculations

When100 cm^3 of a 0.150 mol dm^{-3} solution of aqueous methylamine (CH_3NH_2) is shaken with 75.0 cm^3 of an organic solvent in the separating funnel to allowed to come to equilibrium. Only 25 cm^3 of the aqueous layer is run off and titrated against 0.225MHCl 7.05 cm^3 of HCl was used.

Data for calculations

1. **Volume of aqueous methylamine solution: 100 cm^3**
2. **Initial concentration of methylamine:** 0.150 mol dm^{-3}
3. **Volume of organic solvent:** 75.0 cm^3
4. **Volume of aqueous layer titrated:** 25.0 cm^3
5. **Volume of HCl used for titration:** 7.05 cm^3
6. **Concentration of HCl:** 0.225 mol dm^{-3}

Calculate the partition coefficient of methylamine in the organic solvent and water.

Solution

Step 1: **Write down the equilibrium equation:**

$$CH_3NH_{2(aq)} \rightleftharpoons CH_3NH_2 \text{ (organic solvent)}$$

Step 2: **Write down the K_{pc} expression:**

$$K_{PC} = \frac{[CH_3NH_2\text{ (organic layer)}]}{[CH_3NH_{2(aq)}]}$$

Step 3: **Determine the total moles of methylamine in the original solution.**

Determine the total moles of CH_3NH_2 in the original solution.

$$\text{Total moles } CH_3NH_2 = \frac{0.100 \times 150}{1000}$$

$$= 0.015 \text{ mol}$$

These moles were distributed between the two layers.

Step 4: **Determine the no. of moles methylamine in the aqueous layer.**

$$CH_3NH_{2(aq)} + HCl_{(aq)} \rightarrow CH_3NH_3Cl_{(aq)}$$

25 cm^3 of aqueous layer reacted with 7.05 cm^3 of 0.225 MHCl

1 mol of CH_3NH_2 is: 1 mol of HCl

$$n = M \times V dm^3$$

moles of CH_3NH_2 reacted with HCl solution = moles of HCl solution

$$= 0.225 \times \frac{7.05}{1000}$$

$$= 0.001586 \text{ mol}$$

As 25cm^3 of the aqueous layer was titrated, the 0.001586 mol of methylamine was present in 25cm^3 of the aqueous layer.

So, the moles of methylamine present in 100 cm^3 of aqueous layer = $\frac{0.001586 \times 100}{25}$

$$= 0.00634 \text{ mol}$$

Step 5: **Determine the number of moles of CH_3NH_2 present in the organic layer.**

Mol CH_3NH_2 (organic layer) = mol CH_3NH_2 (total) - mol CH_3NH_2(aqueous layer)

$$= 0.015 - 0.00634$$

$$= 0.00867 \text{ mol}$$

Step 6: **Change the number of moles into concentrations:**

Concentration (CH_3NH_2 in aqueous layer) = $0.0063 \times \frac{1000}{100}$

$$= 0.063 \text{ mol dm}^{-3}$$

Concentration (CH_3NH_2 in organic layer) = $0.0866 \times \frac{1000}{75}$

$$= 0.116 \text{ mol dm}^{-3}$$

Step 7: **Substitute the values into the K_{pc} expression:**

$$K_{PC} = \frac{0.116}{0.0364}$$

$$K_{pc} = 1.83$$

Since the value of K_{pc} is **larger than** 1, methylamine is more soluble in the organic solvent than in water.

CONCEPT ASSESSMENT EXERCISE 3.3

When 2 grams of a solute is shaken with a mixture of 150 cm^3 of water and 20 cm^3 of chloroform. After shaking, 1.5 grams of the solute is found in the chloroform layer. Calculate the partition coefficient.

3.5.2 Factors Affecting the Numerical value of Partition coefficient

The partition coefficient (K_{pc}) indicates how a solute distributes itself between two immiscible phases, usually a non-polar solvent and a polar solvent.

Factors that affect the numerical value of the partition coefficient are:

1. The Polarity of the solute:

A polar solute has a greater affinity for a polar phase (eg, water). This is because polar solutes interact with polar solvents through dipole-dipole or hydrogen bonding interactions.

For example;

A polar solute like ethanol (a polar molecule because of the hydroxyl group) between octanol and water. Ethanol is more soluble in water than octanol, resulting in a higher partition coefficient in favour of the polar phase.

2. The Solvent Polarity:

The nature of the solvents used in the partition plays a decisive role. Non-polar solvents promote the partitioning of non-polar solutes, while polar solvents promote the partitioning of polar solutes. For example;

When a non-polar solute such as benzene is added, its partition coefficient is higher in octanol than in water, because benzene is non-polar and interacts more with non-polar octanol.

3. Temperature:

Temperature can affect the partition coefficient by affecting the solubility and kinetic energy of the solute in both solvents. In general, an increase in temperature can increase the solubility of solutes in polar solvents. For instant;

The partitioning of a polar solute such as aspirin between octanol and water can show different values at different temperatures. At higher temperatures, aspirin is more soluble in water than in octanol.

4. Molecular structure and size

Large solute molecules can interact with solvents differently than smaller molecules. Molecular structure, including functional groups, can also affect the distribution coefficient.

Consider the partitioning of octanol and water between two molecules of similar structure but different sizes, such as ethyl acetate and butyl acetate. A larger butyl acetate molecule may have a lower partition coefficient in favour of the non-polar phase due to increased steric hindrance.

KEY POINTS

- The degree to which different Bronsted acids give off protons is called "acid strength"
- The greater the value of Ka, the stronger the acid".
- The strength of a base is the ability to accept a proton from a solvent
- A buffer solution is a solution, the pH of which does not change significantly when a small amount of acid or base is added to it.
- The bicarbonate ion (HCO_3^-) plays a crucial role in maintaining blood pH through the bicarbonate buffer system.
- The normal pH range of blood is approximately 7.35 –7.45.
- The solubility product is defined as the product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balance chemical equation.
- The phenomenon in which the degree of ionization or solubility of an electrolyte is suppressed by the addition of a highly soluble electrolyte containing a common ion is called the common ion effect.
- The partition coefficient (K_{pc}) is defined as the ratio of the concentrations of a solute in two different immiscible solvents in contact with each other when equilibrium has been established at a particular temperature.
- Nernst`s law states that a solute is distributed between two layers of immiscible solvents so that the ratio of its concentration in each solvent is equal to its solubility.

EXERCISE

1. Multiple Choice Questions (MCQs)

i. Which phenomenon describes a shift in equilibrium due to the addition of an ion already involved in the equilibrium?

a) Le Chatelier's Principle
b) Common Ion Effect
c) Nernst's Law
d) Avogadro's Principle

ii. What property is used to distinguish between strong and weak acids?

a) Molar mass
b) Extent of ionization
c) Density
d) Melting point

iii. Which factor is considered when distinguishing between strong and weak bases?

a) Colour
b) Odor
c) Extent of ionization
d) Solubility

iv. What defines a buffer solution?

a) High concentration of ions
b) Presence of a weak acid and its conjugate base (or a weak base and its conjugate acid)
c) Low pH
d) Absence of ions

v. How can a buffer solution be made?

a) Mixing strong acids and bases

b) Mixing a weak acid and its conjugate base (or a weak base and its conjugate acid)

c) Diluting a strong acid   d) Adding water to a strong base

vi. What role does HCO_3^- play in controlling pH in blood?

a) Neutralization of acids   b) Buffering against changes in pH

c) Catalysing reactions   d) Enhancing oxygen transport

vii. How is the concentration of a slightly soluble salt calculated?

a) Using the solubility product constant (K_{sp})

b) Titration with a strong base

c) Measuring density

d) Conductivity measurement

viii. Which term is used to describe the strength of an acid in terms of its ionization in water?

a) Acid Concentration   b) Acid Dissociation Constant (Ka)

c) Acid Molarity   d) Acid Equilibrium Constant

ix. Which type of solvent would favour the partitioning of a polar solute?

a) Non-polar solvent   b) Hydrophobic solvent

c) Polar solvent   d) Aprotic solvent

x. What is the partition coefficient defined as?

a) Ratio of solute concentration in one solvent to the other

b) Ratio of solute concentration in a single solvent

c) Ratio of solute mass in one solvent to the other

d) Ratio of solute mass in a single solvent

2. Short Answer Questions

i. Explain the common ion effect with a suitable example.

ii. Differentiate between strong and weak acids using the extent of ionization and K_a.

iii. Differentiate between strong and weak bases using the extent of ionization and K_b.

iv. Define a buffer solution and provide an example of how it can be made.

v. How does a buffer solution control pH? Include chemical equations in your explanation.

vi. Describe the uses of buffer solutions in various applications.

vii. Explain how HCO_3^- plays a role in controlling pH in the blood.

viii. Calculate the concentration of a slightly soluble salt given its *solubility product* constant (K_{sp}).

3. Long Answer Questions

i. **Discuss the principles behind the common ion effect, providing two examples to illustrate its application.**

ii. **Compare and contrast strong and weak acids based on their extent of ionization and the value of Ka.**

iii. **Elaborate on the factors that distinguish strong and weak bases, incorporating the concept of ionization and the base dissociation constant (K_b).**

iv. **Provide a comprehensive explanation of buffer solutions, including how they are prepared, how they control pH, and their uses in different scenarios.**

v. **Calculate the pH of an NH_4OH and NH_4Cl buffer solution containing one mole of each. K_b of NH_4OH is 1.8×10^{-5}.** **Ans: 9.26**

vi. **A solute has a partition coefficient $K_{benzene/water}=4$, 100 cm^3 of water is shaken with 100 cm^3 of benzene containing 0.20 mol of the solute. Find the amount of solute that remains in water at equilibrium.** **Ans: 0.04 mol**