

9

ACID-BASE CHEMISTRY**Student Learning Outcomes**

[C-11-A-149 to C-11-A-165]

After studying this chapter, students will be able to:

- Define conjugate acid base pairs. (**Understanding**)
- Identify conjugate acid base pairs in reactions. (**Understanding**)
- Distinguish that Lewis acids accept lone pair, and Lewis bases donate lone pair to make a coordinate covalent bond. (**Understanding**)
- Define mathematically the terms K_w , pH, K_a and pK_a and use them in calculations. (**Application**)
- (K_b and the equation $K_w = K_a \times K_b$ will not be tested).
- Calculate $[H^+_{(aq)}$ and pH values for: (**Application**)
- (a) strong acids (b) strong alkalis (c) weak acids (d) weak alkalies.
- Calculate the $[H_3O^+]$ given the K_a and molar concentration of weak acid. (**Application**)
- Apply the concept of the common ion effect to describe why the solubility of a substance changes when it is dissolved in a solution containing a common ion. (**Application**)
- Calculate the pH of buffer solutions in given appropriate data. (**Application**)
- Construct an expression for K_{sp} . (**Application**)
- Demonstrate the ability to comprehend and effectively apply the concept of solubility product. (K_{sp}). (**Application**)
- Perform calculations using K_{sp} values and concentration of a common ion. (**Application**)
- Calculate concentrations of ions of slightly soluble salts. (**Application**)
- Calculate K_{sp} from concentrations and vice versa. (**Application**)
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. (**Understanding**)
- Apply the concept of conjugate acid and conjugate base on salt hydrolysis. (**Application**)
- Select suitable indicators for acid-alkali titration, given appropriate data (pK_a values will not be used). (**Understanding**)
- Perform acid-base titration to calculate molarity and strength of given sample solutions. (**Application**)

From the earliest days of experimental chemistry, scientists have recognized acids and bases that have distinct characteristic properties. Acids have a sour taste while bases are bitter. Acids and bases change the colour of certain dyes called indicators, such as litmus and phenolphthalein. Acids change litmus from blue to red and phenolphthalein from pink to colourless. Bases change litmus from red to blue and

**Interesting Information**

Acidity in our stomachs is due to excess of HCl. It is treated by taking mild bases such as, baking soda ($NaHCO_3$), milk of magnesia $Mg(OH)_2$ and aluminum hydroxide $Al(OH)_3$



phenolphthalein from colourless to pink. From these colour changes, acids and bases neutralize each other. During neutralization, acids and bases react with each other to produce ionic substances called **salts**.

9.1 BRONSTED-LOWRY CONCEPT

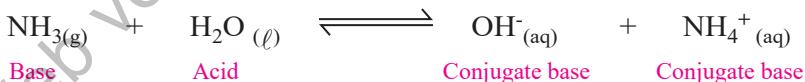
In 1923, the Danish chemist J.N. Bronsted and the English chemist T.M. Lowry independently expanded the Arrhenius theory of acid-base. The Arrhenius theory was limited to the reaction of an acid and base only in the aqueous medium. There are many reactions that occur in solvents other than water or in the absence of any solvent. Bronsted-Lowry pointed out that acid–base reactions can be seen as **proton-transfer reactions** and that acids and bases can be defined in terms of this proton (H^+) donors and proton (H^+) acceptors. According to the Bronsted–Lowry concept, **an acid is the species donating a proton in a proton-transfer reaction and a base is the species accepting the proton.**

When HCl dissolves in water, an H^+ ion (a proton) is transferred from HCl to water, where it becomes attached to a lone pair of electrons on the O atom and forms H_3O^+ . In effect, HCl (the acid) has donated the H^+ and H_2O (the base) has accepted it.



A species formed after a Bronsted base accepts a proton from the acid is called the **conjugate acid**. The hydronium ion (H_3O^+) is the conjugate acid of water. A species formed when an acid donates a proton to a base is called the **conjugate base**. $\text{HCl}-\text{Cl}^-$ and $\text{H}_2\text{O}-\text{H}_3\text{O}^+$ are **conjugate acid-base pairs**.

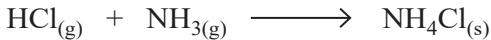
When ammonia dissolves in water, proton transfer also occurs. An H^+ released from H_2O attaches to the N atom's lone pair. NH_4^+ and OH^- are formed. With fewer H^+ , the water molecule becomes OH^- ion:



In this case, H_2O (the acid) has donated the proton and NH_3 (the base) has accepted it. $\text{NH}_3-\text{NH}_4^+$ and $\text{H}_2\text{O}-\text{OH}^-$ are conjugate acid-base pairs.

The above examples show that H_2O is amphoteric in nature because it acts as a base in one case and as an acid in the other. **An amphoteric substance is a species that can act as either an acid and a base (it can lose or gain a proton), depending on the other reactant.**

The Bronsted-Lowry theory can be applied to acids in solvents other than water or even solventless reactions. The reaction between gaseous ammonia and HCl gives solid NH_4Cl .



HCl is an acid because in the reaction it donates a proton to the NH_3 molecule. The NH_3 acts as a base, even though hydroxide ion OH^- is not present, and accepts a proton from the HCl molecule.



Table 9.1 Conjugate Acid-Base Pairs of Common Species

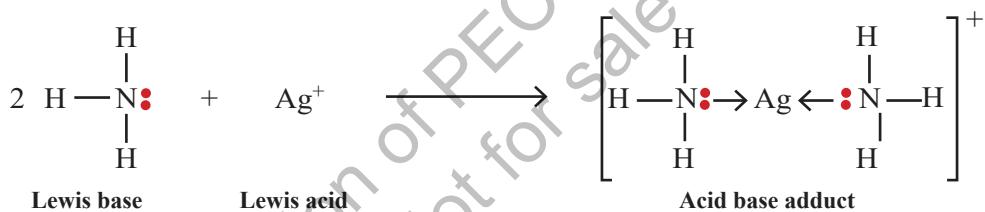
Acid		Base	\rightleftharpoons	Conjugate Acid		Conjugate Base
HNO ₃	+	H ₂ O	\rightleftharpoons	H ₃ O ⁺	+	NO ₃ ⁻
H ₂ SO ₄	+	H ₂ O	\rightleftharpoons	H ₃ O ⁺	+	HSO ₄ ⁻
H ₂ O	+	CO ₃ ²⁻	\rightleftharpoons	HCO ₃ ⁻	+	OH ⁻

9.2 LEWIS CONCEPT OF ACIDS AND BASES

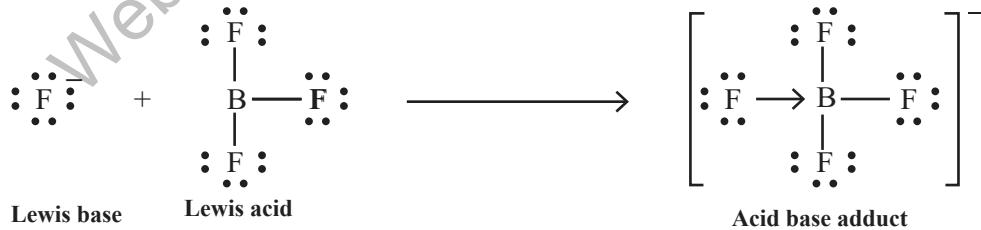
In 1923, G.N. Lewis proposed a generalized definition of acid-base behavior in which acids and bases are identified by their ability to accept or to donate a pair of electrons and form a coordinate covalent bond.

A Lewis acid is any species (molecule or ion) that can accept a pair of electrons and a Lewis base is any species (molecule or ion) that can donate a pair of electrons. A Lewis acid-base reaction occurs when a base donates a pair of electrons to an acid.

In the following reaction, each of two ammonia molecules, Lewis bases, donates a pair of electrons to a positively charged silver ion, the Lewis acid. The sum of charges on the left side is +1, so the acid-base adduct on the right hand side must carry a charge of +1:



The boron atom in boron trifluoride, BF₃, has only six electrons in its valence shell. Since the boron atom has an incomplete octet, it can behave as an electron pair acceptor. As a result, BF₃ is a very good Lewis acid and reacts with many Lewis bases; a fluoride ion is the Lewis base in this reaction, donating one of its lone pairs:

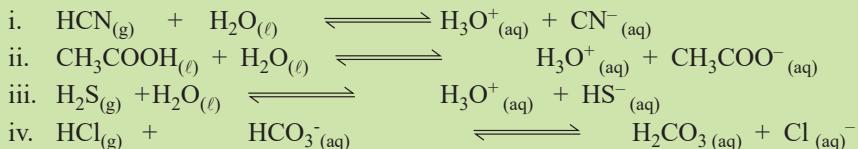


The negative charge on the adduct is the sum of charges on the left hand side of the equation is -1, the sum of charges on the right hand side must also be -1.



Quick Check 9.1

a) Identify the conjugate acid-base pairs in the following reactions:



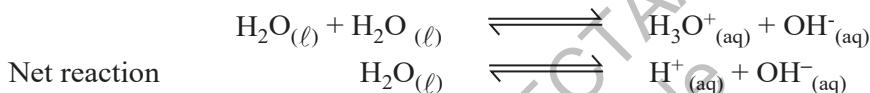
b) Identify the Lewis acid and Lewis base in the reaction between:

- SO_3 and O^{2-}
- HCl and H_2O
- BF_3 and NH_3

Also write down the balanced chemical equation for each reaction and explain.

9.3 IONIC PRODUCT OF WATER

Pure water is a poor conductor of electricity but its conductance is measurable. Water undergoes self-ionization reversibly as follows,



The equilibrium constant for this reaction can be written as follows:

$$K_c = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]} = 1.8 \times 10^{-16} \text{ mol dm}^{-3}$$

The concentration of H_2O , i.e., $[\text{H}_2\text{O}]$ in pure water may be calculated to be 1000 g dm^{-3} divided by 18 g mol^{-1} giving 55.5 mol dm^{-3} . Since, water is present in very large excess and very few of its molecules undergo ionization, so its concentration remains effectively constant. Constant concentration of water is taken on L.H.S. and multiplied with K_c to get another constant called K_w .

$$K_c [\text{H}_2\text{O}] = [\text{H}^+] [\text{OH}^-]$$

$$\text{or } 1.8 \times 10^{-16} \times 55.5 = 1.01 \times 10^{-14} = [\text{H}^+] [\text{OH}^-]$$

This value, i.e. 1.01×10^{-14} is called K_w of water at 25°C .

$$K_c [\text{H}_2\text{O}] = [\text{H}^+] [\text{OH}^-]$$

$$\text{So, } K_w [\text{H}_2\text{O}] = [\text{H}^+] [\text{OH}^-] = 10^{-14} \text{ at } 25^\circ\text{C}$$

K_w is called ionic product of water or dissociation constant of water. The value of K_w increases almost 75 times when temperature is increased from 0°C to 100°C .

For neutral water

$$[\text{H}^+] = [\text{OH}^-]$$

$$\text{or } [\text{H}^+] [\text{H}^+] = 10^{-14}$$

$$[\text{H}^+]^2 = 10^{-14} \quad (\text{at } 25^\circ\text{C})$$



$$[\text{H}^+] = 10^{-7} \text{ mol dm}^{-3}$$

and $[\text{OH}^-] = 10^{-7} \text{ mol dm}^{-3}$

The effect of temperature on K_w is shown in **Table 9.2**. Whenever some quantity of acid or base is added to water, then K_w remains the same, but $[\text{H}^+]$ and $[\text{OH}^-]$ are no more equal.

In case of addition of small amount of acid.

$$[\text{H}^+] > [\text{OH}^-]$$

While in the case of addition of few drops of a base.

$$[\text{OH}^-] > [\text{H}^+]$$

During additions of both, the values of K_w will remain the same, i.e. 10^{-14} at 25°C .

Table 9.2 K_w at various temperature

Temp. ($^\circ\text{C}$)	K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

9.4 pH AND pOH

In all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations. In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH were developed. These two quantities can be calculated as:

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

For neutral water, $\text{pH} = -\log[10^{-7}] = 7$

$$\text{pOH} = -\log[10^{-7}] = 7$$

Also, $\text{pH} + \text{pOH} = 14$

The value of pH normally varies between $0 \rightarrow 14$ at 25°C .

The pH values of some familiar aqueous solutions are shown in **Figure 9.1**. This table helps to understand the acidic or basic nature of commonly used solutions.

Interesting Information!

Solutions of negative pH and having values more than 14 are also known.

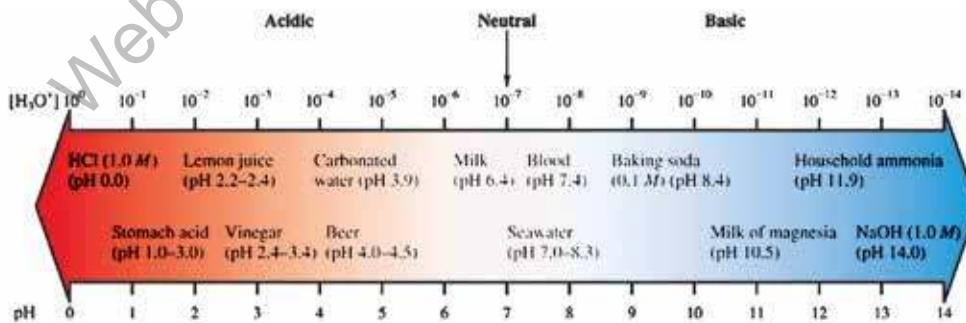


Figure 9.1 pH Values of some common substances

Sample Problem 9.1

In a solution, the pH is 9.2. Determine the ionic product of water K_w at 25°C .



Solution

Calculate the pOH from the pH:

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 9.2$$

$$\text{pOH} = 4.8$$

Find the concentration of H^+ and OH^- ,

Taking antilog of pH and pOH

antilog pH = antilog (9.2)

$$[\text{H}^+] = 10^{-\text{pH}}$$

$$[\text{H}^+] = 10^{-9.2}$$

$$[\text{H}^+] \approx 6.3 \times 10^{-10} \text{ M}$$

Similarly, antilog pOH = antilog (4.8)

$$[\text{OH}^-] = 10^{-\text{pOH}}$$

$$[\text{OH}^-] = 10^{-4.8}$$

$$[\text{OH}^-] \approx 1.6 \times 10^{-5} \text{ M}$$

$$K_w = [\text{H}^+] [\text{OH}^-]$$

$$K_w = (6.3 \times 10^{-10}) (1.6 \times 10^{-5})$$

$$K_w = 1.01 \times 10^{-14}$$

Sample Problem 9.2

The ionic product of water at a certain temperature is $K_w = 1.0 \times 10^{-14}$ at 25 °C. If the concentration of H^+ ions in a solution is $1.0 \times 10^{-7} \text{ M}$. Calculate the concentration of OH^- ions, the pH and pOH of the solution.

Solution

$$K_w = [\text{H}^+] [\text{OH}^-]$$

$$1.0 \times 10^{-14} = (1.0 \times 10^{-7}) [\text{OH}^-]$$

$$[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-7}} = 1.0 \times 10^{-7}$$

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7$$

$$\text{pOH} = -\log[\text{OH}^-]$$

$$\text{pOH} = -\log(1.0 \times 10^{-7})$$

$$\text{pOH} = 7$$



Calculate K_w

$$K_w = [H^+] [OH^-]$$

$$K_w = (6.3 \times 10^{-10}) \times (1.6 \times 10^{-5})$$

$$K_w = 1.008 \times 10^{-14}$$

So, the ionic product of water at the given temperature is $\approx 1.01 \times 10^{-14}$.

Quick Check 9.2

- A solution is prepared by mixing equal volumes of two solutions: one with a pH of 4.0 and another with a pH of 10.0. Calculate the K_w for this mixture at 25°C.
- At a specific temperature, the ionic product of water K_w is 1.0×10^{-14} . If the concentration of OH^- ions in a solution is 2.5×10^{-8} M. Calculate the concentration of H^+ ions and the pH of the solution.
- Copper-plate etching solutions is prepared by diluting concentrated HNO_3 to 0.30 M HNO_3 . Calculate $[H^+]$, pH, $[OH^-]$ and pOH of this solutions at 25 °C.

9.5 IONIZATION CONSTANTS OF ACIDS (K_a)

Acids and bases, when dissolved in water, may or may not be completely dissociated. Many acids are weak electrolytes and ionize to an extent which is much less than 100%. The value of K_a called the dissociation constant of an acid, is the quantitative measure of the strength of the acid. Suppose we have an acid HA dissolved in water,



K_c for the reversible reaction will be written as follows:

$$K_c = \frac{[H_3O^+] [A^-]}{[HA] [H_2O]}$$

$$K_c [H_2O] = \frac{[H_3O^+] [A^-]}{[HA]}$$

Let $K_c [H_2O] = K_a$

$$\text{Hence } K_a = \frac{[H_3O^+] [A^-]}{[HA]}$$

This equation can be used to calculate K_a for any acidic solution if we know the pH or $[H^+]$ of that solution and the initial concentration of the dissolved acid $[HA]$. This can also be used to calculate the equilibrium concentration of H_3O^+ and A^- produced if we know the initial concentration of acid HA and its K_a value.

When $K_a < 10^{-3}$ acid is weak.

$K_a = 1$ to 10^{-3} acid is moderately strong.

$K_a > 1$ acid is strong.

The values of K_a for some acids are given in **Table 9.3**.



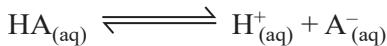
Table 9.3 The values of K_a for some acids

Acid	Dissociation	K_a	Relative strength
HCl	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	very large (10^6)	Very strong
HNO_3	$\text{HNO}_3 \rightleftharpoons \text{H}^+ + \text{NO}_3^-$	very large (10^3)	Very strong
H_2SO_4	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{H}^+ + \text{HSO}_4^-$	very large (10^3)	Very strong
HSO_4^-	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	1.3×10^{-2}	Strong
HF	$\text{HF} \rightleftharpoons \text{H}^+ + \text{F}^-$	6.7×10^{-5}	Weak
CH_3COOH	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	1.85×10^{-5}	Weak
H_2CO_3	$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HS}^-$	4.4×10^{-7}	Weak
H_2S	$\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$	1.0×10^{-7}	Weak
NH_4^+	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3$	5.7×10^{-10}	Weak
HCO_3^-	$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	4.7×10^{-11}	Weak
H_2O	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	1.8×10^{-16}	Very weak

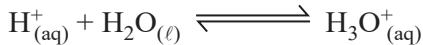
9.5.1 Calculating H_3O^+ Ions from K_a

The weak acids do not completely dissociate in water. Therefore, the concentration of hydronium ions is not equal to the initial concentration of the acid. So, the equilibrium expression is used to calculate the H_3O^+ concentration.

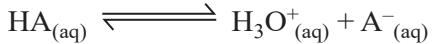
For a weak acid HA, the dissociation in water can be represented as:



In water, H^+ combines with water to form H_3O^+ :



So, the equilibrium equation in terms of $\text{H}_3\text{O}^+(\text{aq})$ is:



Let the initial concentration of the weak acid HA be C mol dm⁻³.

At equilibrium:

$$[\text{H}_3\text{O}^+] = x; \quad [\text{A}^-] = x \quad \text{and} \quad [\text{HA}] = C - x$$

The expression for the acid dissociation constant (K_a) is:



$$K_a = \frac{[H_3O^+] [A^-]}{[HA]}$$

Substitute the equilibrium concentrations into this expression:

$$K_a = \frac{x \times x}{C - x} = \frac{x^2}{C - x}$$

For weak acids, x is usually very small compared to C , so $C - x \approx C$. Therefore, the expression simplifies to:

$$K_a \approx \frac{x^2}{C}$$

Taking the square root of both sides:

$$x \approx \sqrt{K_a \times C}$$

Thus, the concentration of H_3O^+ is given by:

$$x \approx \sqrt{K_a \times C}$$

Sample Problem 9.3

Calculate the concentration of $[H_3O^+]$ in a 0.1 M (mol dm^{-3}) solution of acetic acid $[\text{CH}_3\text{COOH}]$, given that the acid dissociation constant K_a is 1.8×10^{-5} .

Solution

$$[H_3O^+] \approx \sqrt{K_a \times C}$$

$$[H_3O^+] \approx \sqrt{1.8 \times 10^{-5} \times 0.1}$$

$$[H_3O^+] \approx \sqrt{0.18 \times 10^{-6}}$$

$$[H_3O^+] \approx 1.34 \times 10^{-3} \text{ M (mol dm}^{-3}\text{)}$$

The concentration $[H_3O^+]$ in the solution is approximately $1.34 \times 10^{-3} \text{ mol dm}^{-3}$.

Quick Check 9.3

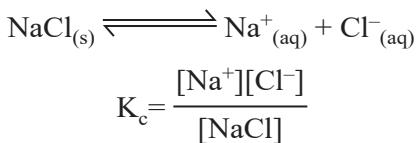
- The pH of a 0.10 M solution of formic acid, HCOOH , at 25°C is 2.38. Calculate K_a for formic acid at this temperature.
- Calculate the concentration of $[H_3O^+]$ in a 0.1 M solution of nitrous acid $[\text{HNO}_2]$, given that the acid dissociation constant K_a is 4×10^{-4} .
- A vinegar sample is found to have 0.837 M CH_3COOH . Its hydronium ion concentration is found to be $3.86 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate K_a for acetic acid.

9.6 COMMON ION EFFECT

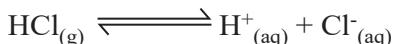
The suppression of ionization of a weak electrolyte by adding a common ion to it is called **common ion effect**. We are familiar with purification of sodium chloride by passing hydrogen chloride gas through brine (saturated solution of NaCl).



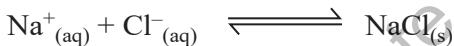
Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:



HCl also ionizes in solution:

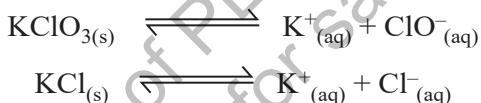


On passing HCl gas, concentration of Cl^- ion is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant. This type of effect is called the common ion effect. The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

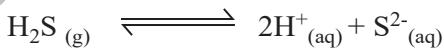


More examples of common ion effect

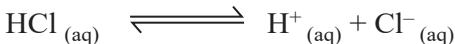
- i. The solubility of a less soluble salt KClO_3 in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of KClO_3 is suppressed and it settles down as precipitate.



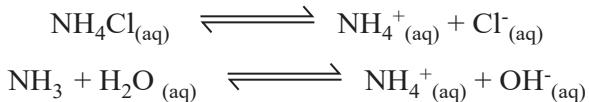
- ii. Similarly, the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way, low concentration of S^{2-} ion is produced.



This low concentration of S^{2-} ions helps to do the precipitation of radicals of II group basic radicals during salt analysis.



- iii. An addition of NH_4Cl in NH_3 solution suppresses the concentration of OH^- due to the presence of a large excess of NH_4^+ from NH_4Cl . Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as a group reagent in III group basic radicals for salt analysis.



Common ion effect finds many applications in the qualitative analysis and the preparation of buffers.



9.7 BUFFER SOLUTIONS

The solutions which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions. They have a specific constant value of pH and their pH values do not change on dilution and even keeping for a long time.

Buffer solutions are mostly prepared by mixing two substances.

- By mixing a weak acid and its salt with a strong base. Such solutions give acidic buffers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of acidic buffers.
- By mixing a weak base and its salt with a strong acid. Such solutions will give basic buffers with pH more than 7. Mixture of NH_4OH and NH_4Cl is one of the best examples of basic buffers.

Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa . CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH_3COONa which is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^- .



If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increases. The **Table 9.4** tells us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid as compared to CH_3COONa , lesser is the pH of solution.

Table 9.4 Effect of addition of acetate ions on the pH of acetic acid solution

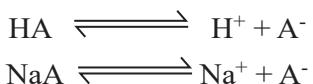
[CH_3COOH] (mol dm ⁻³)	[CH_3COO^-] (mol dm ⁻³)	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Actually, a buffer mentioned above is a large reservoir of CH_3COOH and CH_3COO^- components. When an acid or H_3O^+ ions are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH_3COOH being a weak acid will prefer to remain undissociated. Similarly, the buffer solution consisting of NH_4Cl and NH_4OH , can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.



9.7.1 Calculating the pH of a Buffer

How a buffer of definite pH can be prepared. Consider a weak acid HA and its salt NaA with a strong base say NaOH. The reversible reactions for dissociation of HA and NaA are as follows:



pH of a buffer solution can be calculated by using Henderson equation as given below:

$$\text{pH} = \text{pK}_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

Interchanging the numerator and denominator, the sign of log changes.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

This relationship is called **Henderson's equation**. This equation shows that two factors evidently govern the pH of a buffer solution. First is the pK_a of the acid used and the second is the ratio of the concentrations of the salt and the acid. The best buffer is prepared by taking equal concentration of salt and acid. So, pH is controlled by pK_a of the acid. For example, for acetic acid – sodium acetate buffer, if $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COONa}]$

$$\text{Then } \text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = \text{pK}_a + \log (1)$$

$$\text{So, } \text{pH} = \text{pK}_a + 0 = \text{pK}_a$$

$$\text{pH} = 4.74.$$

It means that the pH of this buffer is just equal to the pK_a of the acid.

Quick Check 9.4

- Explain the impact of common ion effect on solubility.
- To a saturated solution of AgCl, some of NaCl solution was added.
 - State the effect of the concentration of Ag^+ on the equilibrium.
 - Explain your answer with respect to the common ion effect.
- How does a buffer maintain pH stability?
- Calculate the pH of a buffer consisting of 0.50 M HF and 0.45 M of a fluoride (F^-) salt before and after addition of 0.40 g NaOH to 1.0 dm³ of the buffer (K_a of HF = 6.8×10^{-4}).
- Calculate the pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 molar acetic acid solutions are present. K_a for CH_3COOH is 1.85×10^{-5}



Interesting Information!

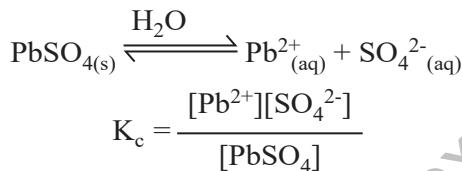
The body's blood buffering system, involving bicarbonates, helps maintain a stable pH. The compositions of injections are buffered to ensure that no change in blood's pH occur.



9.8 SOLUBILITY PRODUCT

When a soluble ionic compound is dissolved in water, like NaCl, it dissociates completely into ions. But for slightly soluble salts the dissociation is not complete at equilibrium stage. For example, when PbSO₄ is shaken with water the solution contains Pb²⁺, SO₄²⁻ and undissociated PbSO₄. It means that equilibrium exists between solid solute, PbSO₄ and the dissolved ions, Pb²⁺ and SO₄²⁻.

Lead sulphate is a well-known sparingly soluble compound and it dissociates to a very small extent like PbCl₂.



Being a sparingly soluble salt, the concentration of lead sulphate (PbSO₄) almost remains constant. Bring [PbSO₄] on L.H.S. with K_c.

$$K_c [\text{PbSO}_4] = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

if K_c [PbSO₄] = K_{sp}

then K_{sp} = [Pb²⁺][SO₄²⁻] = 1.6 × 10⁻⁸ at 25°C

K_{sp} is called the solubility product of PbSO₄. It is the product of molar solubilities of two ions at equilibrium stage.

Similarly, for another sparingly soluble salt, PbCl₂. K_{sp} = [Pb²⁺][Cl⁻]²

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent. So, the solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation. The value of K_{sp} is a measure of the dissociation of sparingly soluble salt.

The following **Table 9.5** shows the K_{sp} values of some slightly soluble ionic compounds.

Table 9.5 K_{sp} values for some ionic compounds

Salt	Ion Product	K _{sp}	Salt	Ion Product	K _{sp}
AgBr	[Ag ⁺][Br ⁻]	5.0 × 10 ⁻¹³	CuS	[Cu ²⁺][S ²⁻]	8 × 10 ⁻³⁴
AgCl	[Ag ⁺][Cl ⁻]	1.8 × 10 ⁻¹⁰	Fe ₂ S ₃	[Fe ³⁺] ² [S ²⁻] ³	1.4 × 10 ⁻⁸⁵
Al(OH) ₃	[Al ³⁺][OH ⁻] ³	3 × 10 ⁻³⁴	MgCO ₃	[Mg ²⁺][CO ₃ ²⁻]	3.5 × 10 ⁻⁸
BaCO ₃	[Ba ²⁺][CO ₃ ²⁻]	1.1 × 10 ⁻¹⁰	MnS	[Mn ²⁺][S ²⁻]	3 × 10 ⁻¹¹
CaCO ₃	[Ca ²⁺][Ca ₃ ²⁻]	3.3 × 10 ⁻⁹	PbCrO ₄	[Pb ²⁺][CrO ₄ ²⁻]	2.3 × 10 ⁻¹³
CaF ₂	[Ca ²⁺][F ⁻] ²	3.2 × 10 ⁻¹¹	PbSO ₄	[Pb ²⁺][SO ₄ ²⁻]	1.6 × 10 ⁻⁸



9.8.1 Applications of solubility product

a) Determination of solubility from K_{sp}

For this purpose, we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions is determined. **Table 9.6** shows the relationship between the K_{sp} values and the solubility of some sparingly soluble compounds.

Table 9.6 The relation between solubility and solubility products of some salts

Formula	No. of ions	K_{sp}	Solubility gdm ⁻³
PbSO ₄	2	1.69×10^{-4}	1.3×10^{-4}
Ca(OH) ₂	3	6.5×10^{-6}	1.175×10^{-2}
CaF ₂	3	3.2×10^{-11}	2.0×10^{-4}
Ag ₂ CrO ₄	3	2.6×10^{-12}	8.7×10^{-5}

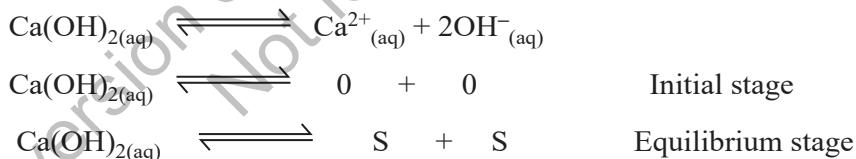
Sample Problem 9.4

Ca(OH)₂ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6} . Calculate the solubility of Ca(OH)₂.

Solution

Let the solubility be represented by S in terms of mol dm⁻³.

The balanced equation is:



The concentration of OH⁻ is double than the concentration of Ca²⁺, so

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = S \times (2S)^2$$

$$4S^3 = 6.5 \times 10^{-6}$$

$$S^3 = \frac{6.5 \times 10^{-6}}{4}$$

$$S = (1.625)^{1/3} \times 10^{-2}$$

$$S = 1.18 \times 10^{-2} \text{ mol dm}^{-3}$$

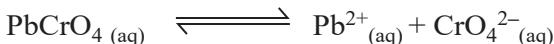
Hence, at equilibrium stage 1.18×10^{-2} mol dm⁻³ of Ca²⁺ and $2 \times 1.18 \times 10^{-2}$ mol dm⁻³ = 2.36×10^{-2} mol dm⁻³ OH⁻ are present in the solution. In this way, we have calculated the individual concentrations of Ca²⁺ and OH⁻ ions from the solubility product of Ca(OH)₂.

b) Common Ion Effect

The presence of a common ion decreases the solubility of a slightly soluble ionic compound.



In order to explain it, consider a saturated solution of PbCrO_4 , which is a sparingly soluble ionic salt.



Now add Na_2CrO_4 which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble PbCrO_4 . So equilibrium is shifted to the left to keep K_{sp} constant.

c) Predicting Precipitation

The solubility product can also help in predicting whether the precipitation of a salt will occur or not. For example, the solubility product of CaSO_4 is 2×10^{-5} . If we add 10^{-2} mol dm^{-3} solution Ca^{2+} to 10^{-2} mol dm^{-3} solution of SO_4^{2-} ions at 25°C . The concentrations of each ionic species can be calculated as

$$\begin{aligned} [\text{Ca}^{2+}] &= [\text{SO}_4^{2-}] = \frac{10^{-2}}{2} = 5.0 \times 10^{-3} \text{ mol dm}^{-3} \\ [\text{Ca}^{2+}][\text{SO}_4^{2-}] &= 5.0 \times 10^{-3} \text{ mol dm}^{-3} \times 5.0 \times 10^{-3} \text{ mol dm}^{-3} \\ &= 2.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \\ &= 2.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} > K_{sp} \text{ of } \text{CaSO}_4 \end{aligned}$$

As the ionic product of concentrations is greater than K_{sp} , therefore CaSO_4 will precipitate out.

Ionic Product	Type of Solution	Precipitation
$> K_{sp}$	Supersaturated	Yes
$= K_{sp}$	Saturated	No
$< K_{sp}$	Unsaturated	No

Quick Check 9.5

- The solubility product constant (K_{sp}) of silver chloride (AgCl) is 1.77×10^{-10} at 25°C . A solution already contains M of 0.10 M AgCl . Find the solubility of AgCl in a solution if 0.10 M sodium chloride (NaCl) is added.
- Predict whether CaSO_4 will be precipitated or not when 10^{-3} mol dm^{-3} of each of Ca^{2+} and SO_4^{2-} is mixed together.
- Solution of potassium carbonate is basic.
 - Explain why the solution is alkaline.
 - Also give the equation for the hydrolysis of the above salt.



Interesting Information!

The shell of this nautilus is composed mainly of calcium carbonate. The nautilus adjusts conditions so shell material is formed when the concentration of calcium ions and carbonate ions in seawater are high enough to precipitate calcium carbonate.



9.9 SALT HYDROLYSIS

When a salt dissolves in water, it dissociates into its constituent ions. These ions can interact with water, affecting the solution's pH depending on the nature of the acid and base from which the salt is derived.

9.9.1 Salts of Strong Acids and Strong Bases

For salts derived from strong acids and strong bases (e.g., sodium chloride, NaCl). The conjugate base of a strong acid (e.g., Cl⁻ from HCl) is very weak and does not significantly react with water. The conjugate acid of a strong base (e.g., Na⁺ from NaOH) is also very weak and does not significantly react with water.



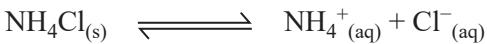
Na⁺ is the conjugate acid of NaOH (a strong base) and does not affect the pH.

Cl⁻ is the conjugate base of HCl (a strong acid) and does not affect the pH.

The solution remains neutral.

9.9.2 Salts of Strong Acids and Weak Bases

For salts derived from strong acids and weak bases (e.g., ammonium chloride, NH₄Cl), The conjugate base of the strong acid (e.g., Cl⁻) does not react with water. The conjugate acid of the weak base (e.g., NH₄⁺ from NH₃) reacts with water to produce H₃O⁺ ions, making the solution acidic.



NH₄⁺ is the conjugate acid of NH₃ (a weak base) and reacts with water:



Cl⁻ is the conjugate base of HCl (a strong acid) and does not affect the pH.

The solution is acidic due to the NH₄⁺ ion.

9.9.3 Salts of Weak Acids and Strong Bases

The example of salt of weak acid and strong base is sodium acetate.



CH_3COO^- is the conjugate base of CH_3COOH (a weak acid) and reacts with water:

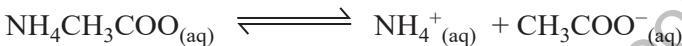


Na^+ is the conjugate acid of NaOH (a strong base) and does not affect the pH. The solution is basic due to the CH_3COO^- ion.

9.9.4 Salts of Weak Acids and Weak Bases

For salts derived from weak acids and weak bases (e.g., ammonium acetate, $\text{CH}_3\text{COO}\text{NH}_4$):

The conjugate acid (NH_4^+) and the conjugate base (CH_3COO^-) both affect the pH.



NH_4^+ hydrolyzes to produce H_3O^+ .



CH_3COO^- hydrolyzes to produce OH^- .



The resultant pH of the solution depends on the relative strengths of the conjugate acid and conjugate base. The solution may be acidic, basic, or nearly neutral, depending on which reaction is more dominant.

9.10 ACID–BASE INDICATORS

An indicator is a substance that changes colour to mark a titration's endpoint. Acid-base indicators exhibit one colour in acid and another in base. Most indicators used in acid-base titration are weak organic acids or bases. In solution, a weak-acid indicator (HIn) can be represented by the equation below:



In^- is the symbol of the anion part of the indicator. Because the reaction is reversible, both HIn and In^- are present. The colours displayed result from the fact that HIn and In^- have different colours.

In acidic solutions, any In^- ions that are present act as Brønsted bases and accept protons from the acid. The indicator is then present in largely unionized form, HIn . In basic solutions, the OH^- ions from the base combine with the H^+ ions produced by the indicator. The indicator molecules further ionize to equalize the loss of H^+ ions. The indicator is thus present largely in the form of its anion, In^- . The solution now shows the base-indicating colour, which for litmus is blue.

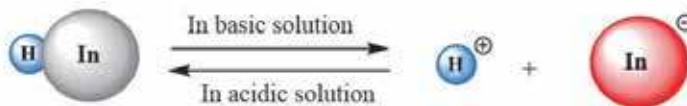


Figure 9.2 Unionized and ionized acid-base indicators and their ionised forms exist in an equilibrium



Different indicators change colour at different pH values. The colour depends on the relative amounts of HIn and In^- at a given pH. For example, methyl red changes from red to yellow between pH 4.4 and 6.2. At pH 4.4, the indicator exists mostly as HIn molecules, which appear red in the solution. The indicator ranges are given below for some of the commonly used indicators as shown in **Figure 9.3**.

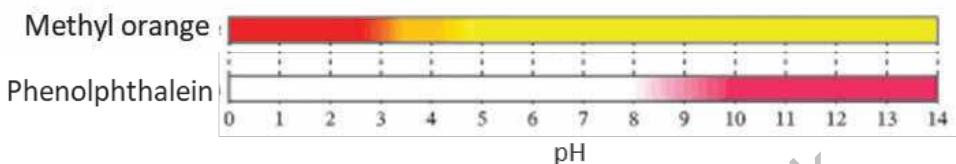


Figure 9.3 Range and colour changes of some common Acid-Base indicators

9.10.1 Selecting a Suitable Indicator

The two general criteria for an indicator to be used in a titration are:

- The pH at the end of the titration should be close to the indicator's neutral point.
- The indicator should indicate a sharp colour change near the equivalence point of the titration.

Each pH indicator changes colour over a defined range of pH, known as the indicator range. An indicator changes colour over a range of about 2 pH units.

9.10.2 Titration Curve and Equivalence Point

A pH curve is a graph of the pH of the solution versus the volume of titrant added. **The equivalence point is the point at which the amount of titrant added is just enough to neutralize the analyte solution completely.**

Titration curves show how the pH of an acidic or basic solution changes as a basic or acidic solution is added to it. We can use the titration curve to choose an indicator that will show when the titration is complete and we reach the equivalence point. The end point of the titration occurs when the indicator changes colour. We choose an indicator with an end point close to the equivalence point.

1. Strong Acid-Strong Base Titration Curve

As an example of a strong acid-strong base titration, let's consider the titration of HCl with NaOH. Initially, the

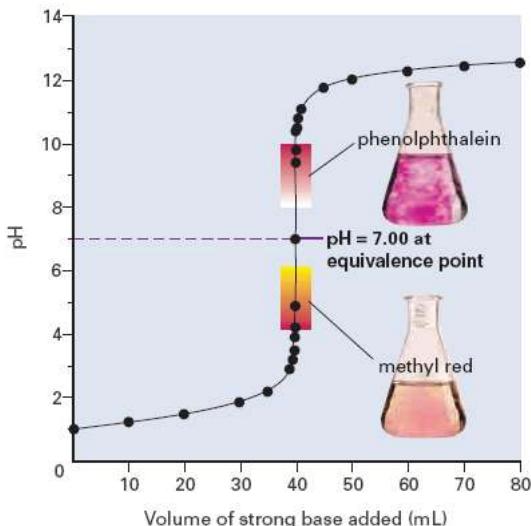


Figure 9.4 Strong acid-strong base titration curve



solution contains only the strong acid. Since the acid is strong, it completely dissociates, leading to a high concentration of H^+ ions and the pH is very low.

As NaOH is added, OH^- ions from NaOH begin to neutralize the H^+ ions from HCl and pH of the solution rises.

The equivalence point is reached when the amount of OH^- added is stoichiometrically equal to the amount of H^+ originally present in the acid. The pH at the equivalence point in a strong acid-strong base titration is 7.0. The titration curve at this stage shows a steep rise in pH, changing quickly from acidic to neutral. The pH value at the endpoint changes about from 4.0 to 10.0. These titrations have a pH of 7.0 at equivalence, so, such phenolphthalein as indicator can be used as they show different colours in this range.

2. Strong Acid-Weak Base Titration Curve

Consider the titration of aqueous NH_3 with HCl . Initially, the solution contains only the weak base and it only partially dissociates, with a lower concentration of OH^- ions compared to a strong base. The initial pH will be greater than 7 but lower than the pH of a strong base. As HCl is added, the concentration of OH^- decreases, causing a further decrease in pH.

Before reaching the equivalence point, the solution is in a buffer-like region where the pH changes more gradually. The presence of the weak base and its conjugate acid (from the salt formed) creates a buffering effect, which helps to moderate the pH change as the base is added.

The pH at the equivalence point will be less than 7 ($\text{pH} = 5.27$) because the conjugate acid slightly dissociates, releasing H^+ ions making the solution acidic ($\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$).

After the equivalence point, the pH of the solution decreases rapidly. This is because the strong acid dissociates completely in water, providing a high concentration of hydrogen ions (H^+), which significantly lowers the pH. Methyl orange has its colour change in this range, therefore, it can be used as an indicator for strong acid-weak base titrations.

Table 9.7 pH ranges of common indicators

Indicators	Acid colour	Base colour	pH Range	Type of Titration
Methyl orange	orange	yellow	3.2-4.5	strong acid-strong base strong acid-weak base
Phenolphthalein	colourless	red	8.2-10.0	strong acid-strong base



Quick Check 9.6

- Differentiate end point and equivalent point.
- Explain how an indicator changes its colour in acidic and basic solution.
- Suggest a suitable indicator for weak acid and strong base titration.
- Suggest a suitable indicator for weak acid and weak base titration.

EXERCISE**MULTIPLE CHOICE QUESTIONS**

Q.1 Four choices are given for each question. Select the correct choice.

I. Given the following reaction:



- NH_3 is the acid, H_2O is the base.
- NH_3 is the base, H_2O is the acid.
- NH_4^+ is the base, OH^- is the acid.
- H_2O is the base, OH^- is the acid.

II. The pH of 10^{-3} mol dm $^{-3}$ of an aqueous solution of H_2SO_4 is:

- 3.0
- 2.7
- 2.0
- 1.5

III. The solubility product of AgCl is 2.0×10^{-10} mol 2 dm $^{-6}$. The maximum concentration of Ag^+ ions in the solution is:

- 2.0×10^{-10} mol dm $^{-3}$
- 1.41×10^{-5} mol dm $^{-3}$
- 1.0×10^{-10} mol dm $^{-3}$
- 4.0×10^{-20} mol dm $^{-3}$

IV. Which indicator is typically used for titrations involving strong acids and strong bases?

- Methyl red
- Phenolphthalein
- Bromothymol blue
- Litmus solution

V. Which of the following is the conjugate base of water?

- $\text{OH}^{-\text{(aq)}}$
- $\text{H}^{+\text{(aq)}}$
- $\text{H}_2\text{O}_{\text{(l)}}$
- $\text{H}_3\text{O}^{+\text{(aq)}}$

VI. Which of the following is a Lewis acid but not a Bronsted-Lowry acid?

- HCl
- NH_3
- AlCl_3
- H_2O



VII. In an acid-base titration, the equivalence point is reached when:

- a) pH of the solution is 7.0.
- b) The indicator changes colour.
- c) Equal volumes of acid and base have been added.
- d. The reaction stops.

VIII. If the concentration of Cl^- ion in a solution is increased, the solubility of silver chloride (AgCl) will:

- a) Decrease
- b) Increase
- c) Remain unchanged
- d) Become zero

IX. Which of the following pairs of substances can act as a conjugate acid-base pair according to the Bronsted-Lowry theory?

- a) HCl and NaOH
- b) NH_3 and NH_4^+
- c) H_2O and H_2SO_4
- d) H_2O and CH_4

X. If the pH of a solution is 11, what is the $[\text{OH}^-]$ concentration in the solution?

- a) $1 \times 10^{-3} \text{ M}$
- b) $1 \times 10^{-11} \text{ M}$
- c) $1 \times 10^{-2} \text{ M}$
- d) $1 \times 10^{-14} \text{ M}$

XI. Which of the following pairs forms a buffer solution?

- a) HCl and NaCl
- b) CH_3COONa and CH_3COOH
- c) NaOH and HCl
- d) NH_3 and Na_2SO_4

SHORT ANSWER QUESTIONS**Q.2 Attempt the following short-answer questions:**

- a. Define the following with an example for each:
 - i) Ionization constant
 - ii) Solubility product
 - iii) Common ion effect
 - iv) Acid-base Indicator
- b. Differentiate between:
 - i) Hydrolysis and dissolution
 - ii) Acidic and basic buffer solutions
- c. Explain the concept of conjugate acid-base pairs. How are they related in terms of proton transfer?
- d. What is the relationship between the strength of an acid and the strength of its conjugate base?
- e. For the following three reactions, identify the reactants that are Arrhenius bases, Bronsted-Lowry bases, and/or Lewis bases. State which type(s) of bases each reactant is. Explain your answers.
 - i) $\text{NaOH}_{(\text{s})} \rightleftharpoons \text{Na}^{+}_{(\text{aq})} + \text{OH}^{-}_{(\text{aq})}$
 - ii) $\text{HF}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{F}^{-}_{(\text{aq})} + \text{H}_3\text{O}^{+}_{(\text{aq})}$
 - iii) $\text{H}^{+}_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightleftharpoons \text{NH}_4^{+}_{(\text{aq})}$



- f. An amphoteric substance can behave as either an acid or a base. Identify whether water behaves as an acid or a base in each of the following reactions.
- $\text{H}_2\text{O} + \text{HCl} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$
 - $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$
 - $\text{HNO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NO}_3^-$
 - $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$
- g. Which salt would you expect to dissolve more readily in acidic solution: Barium carbonate or Copper sulfide? Explain. ($K_{sp}(\text{BaCO}_3) = 1.1 \times 10^{-10}$, $K_{sp}(\text{CuS}) = 8 \times 10^{-34}$)
- h. Why does common ion effect decrease solubility of a less soluble salt?
- i. State the basic principle of solubility product. Mention factors affecting solubility product.
- j. Prove by equations what happens when Na_2CrO_4 is added to saturated solution of PbCrO_4 .
- k. According to the Lewis acid-base concept, boron trifluoride (BF_3) can act as an acid. Is this statement correct?
- l. If the concentration of hydrogen ions in a solution is 1×10^{-5} M, what is the pH of the solution?

DESCRIPTIVE QUESTIONS

- Q.3** Describe the Bronsted-Lowry theory of acids and bases. Provide examples of conjugate acid-base pairs and explain clearly their relationship.
- Q.4** Define the Lewis theory of acids and bases. How does this theory differ from the Bronsted-Lowry theory? Give examples of Lewis acids and bases that do not involve proton transfer.
- Q.5** Discuss applications and implications of the common ion effect in various fields.
- Q.6** What is the solubility product for sparingly soluble salts. Give its two applications.
- Q.7** Describe the general shape of a titration curve for a strong acid titrated with a strong base. How can you identify the equivalence point on this titration curve?

NUMERICAL PROBLEMS

- Q.8** A buffer solution has a pH of 5.0. It is made from a weak acid HA with a pK_a of 4.8. What is the ratio of the concentration of the conjugate base $[\text{A}^-]$ to the concentration of the weak acid $[\text{HA}]$ in this buffer?
- Q.9** Calculate the solubility of a sparingly soluble salt lead (II) iodide (PbI_2) in water. It has $K_{sp} = 1.4 \times 10^{-8}$.
- Q.10** The molar solubility of silver chromate (Ag_2CrO_4) in pure water at 298 K is 6.5×10^{-5} mol dm⁻³. Calculate the K_{sp} of silver chromate at this temperature.

