CHAPTER 9

ACIDS - BASES CHEMISTRY

SLOs: After completing this lesson, the student will be able to:

1. Define conjugate acid-base pairs.
2. Identify conjugate acid-base pairs in reactions.
3. Apply the concept of conjugate acid and conjugate base on salt hydrolysis.
4. Define mathematically the terms pH, K_a, pK_a, and K_w and use them in calculations (K_b and the equation $K_w = K_a \times K_b$ will not be tested).
5. Calculate $[H^+]$ and pH values for: (a) strong acid (b) strong alkalis (c) weak acids (d) weak alkalis.
6. Distinguish that Lewis acids accept lone pair, and Lewis bases donate lone pair to make a coordinate covalent bond.
7. Calculate the pH of buffer solutions in given appropriate data.
8. Demonstrate the ability to comprehend and effectively apply the concept of solubility product (K_{sp}).
9. Construct an expression for K_{sp}.
10. Calculate K_{sp} from concentrations and vice versa.
11. 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.
12. Perform calculations using K_{sp} values and concentration of a common ion.
13. Use the concept of hydrolysis to explain why aqueous solutions of some salts acidic or basic.
14. Calculate the $[H_3O^+]$ given the Ka and molar concentration of weak acids.
15. Calculate concentrations of ions of slightly soluble salts.
16. Perform acid-base titrations to calculate molarity and strength of given sample solutions.
17. Select suitable indicators for acid-alkali titrations, appropriate data (pK_a values will not be used).

Acids were first identified as substances with a sour taste. Vinegar tastes sour because it is a dilute solution of acetic acid. Citric acid is responsible for the sour taste of lemon. Bases, sometimes called alkalis, are characterized by their bitter taste and slippery feel. Commercial preparations for unclogging drains are highly basic. Salt is an ionic substance formed by neutralizing an acid and a base. Acid-base chemistry is important in many everyday applications. The effect of acids on living things has become particularly important in recent years due to acid rain. Acids are classified as (i) mineral acids and (ii) organic acids. Organic acids are much weaker than mineral acids. Organic acids are mostly found in vegetables, fruits, and other things. Some of the common organic acids and their occurrence in different substances are:

Organic acids	**Where it is found**
Lactic acid	Sour Milk
Citric acid	Citrus fruits like lemons, oranges
Formic acid	Insect bites
Tartaric acid	Grape juice
Maleic acid	Apples and pears

The presence of water is essential for the formation of H^+, for example HCl is covalent in nature and does not form H^+ ions. However, it forms H_3O^+ ions in the presence of H_2O.

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Bases form a class of chemical substances including metal oxides and hydroxides. A soluble base is called an alkali and forms OH^- ions when dissolved in H_2O.

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

$Ca(OH)_2$ is an alkali and a base.

Alkalis are important in soap and detergent manufacture. Caustic soda (NaOH) is used for this purpose.

The ionic substance obtained as a result of the neutralization of acids and bases are called salts.

e.g. $$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{NaCl} + H_2O$$

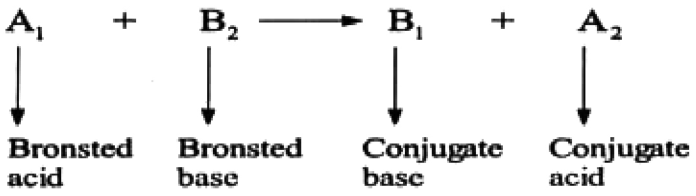
A salt may be neutral, acidic or basic.

9.1 CONJUGATE ACID - BASE PAIRS

A conjugate acid is a species formed as a result of the acceptance of a proton by a base. A conjugate base is the species that remains after donating a proton from an acid. In an acid-base reaction, the acid forms a base (conjugate) and the base, having accepted a proton, forms a conjugate acid. The acid-base reaction is as shown

DO YOU KNOW

A strong acid produces a relatively weak conjugate base. Likewise a strong base produces a relatively weak conjugate acid.

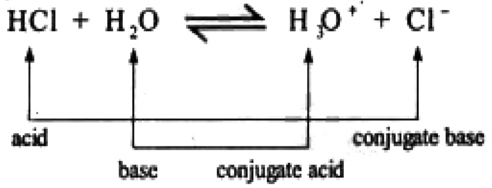


$$A_1 + B_2 \longrightarrow B_1 + A_2$$

The conjugate acid-base pairs are species on opposite sides of an equation that differ by a proton. The weaker acids have stronger conjugate bases and stronger acids have weaker conjugate bases.

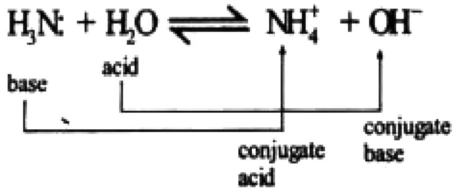
Examples

Ionization of HCl in water;



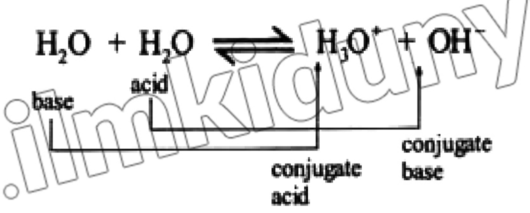
$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

Ionization of NH_4OH in water;



$$H_3N: + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Ionization of H_2O;



$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

The water is amphoteric in nature i.e. it is acidic as well as basic in nature.

Particular Examples of Conjugate Acid-Base Pairs:

$$A_1 + B_2 \rightleftharpoons B_1 + A_2$$

$$HCl + H_2O \rightleftharpoons Cl^{1-} + H_3O^{1+}$$

$$HCl + NH_3 \rightleftharpoons Cl^{1-} + NH_4^{1+}$$

$$HNO_3 + H_2O \rightleftharpoons NO_3^{1-} + H_3O^{1+}$$

$$NH_4^{+1} + H_2O \rightleftharpoons NH_3 + H_3O^{1+}$$

$$H_2O + H_2O \rightleftharpoons OH^{1-} + H_3O^{1+}$$

$$H_2O + CO_3^{2-} \rightleftharpoons OH^{1-} + HCO_3^{1-}$$

$$HClO_4 + H_2O \rightleftharpoons ClO_4^{1-} + H_3O^{1+}$$

A_1, B_1, and B_2, A_2, are known as conjugate acid-base pairs.

9.2 Lewis Concept of Acids and Bases:

Certain substances like SO_2, CO_2, CaO, BF_3 etc. behave as acids or bases although they do not have ability to donate or accept protons. Nature of such substances cannot be explained by Arrhenius theory or the Bronsted-Lowry theory.

In 1923, G.N Lewis proposed an acid base theory that focuses on reaction. This concept is more general than either the Arrhenius theory or the Bronsted - Lowery theory.

A Lewis acid is substance that can accept a pair of electrons to form a coordinate covalent bond.

A Lewis base is a substance that can donate a pair of electrons to form a coordinate covalent bond.

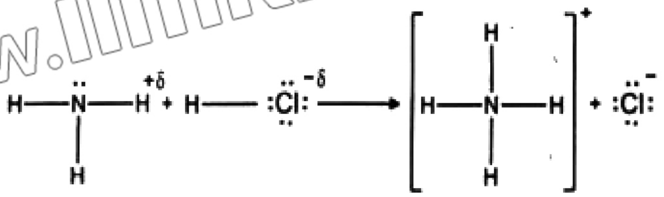
In a Lewis acid-base reaction a coordinate covalent bond is formed between the acid and the base. Consider the following reaction.

Electron pair acceptor Electron pair donor

(i) **Which species is donating an electron pair?**
(ii) **Which species is accepting an electron pair?**
(iii) **Which species is a Lewis acid?**

(iv) Which species is a Lewis base ?

This theory can explains gas phase neutralization reactions.

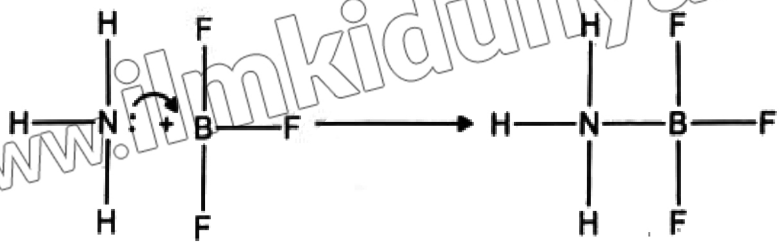


Nitrogen atom in ammonia donates an electron pair to H- atom in HCl. Which species in Lewis acid?HCl or NH_3.

The Lewis structure demands that the central atom or atom of Lewis acid has a deficiency of an electron pair and can accommodate an unshared electron pair. On the other hand, the central atom of a Lewis base has complete octet possessing one or more unshared electron pairs. Hence base has an ability to donate an unshared electron pair.

Example 9.1: Classifying substances as Lewis acids or Lewis bases.

Identify the Lewis acidand Lewis base in the following reactions.

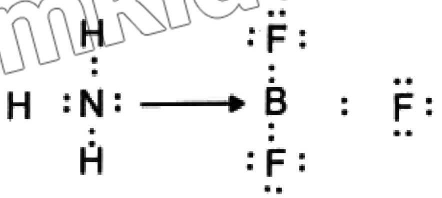


Problem Solving Strategy

1. Draw electronic structures of both the species.
2. Look for the species that has a lone - pair of electron or negative charge. Such a species has complete octet, so it does not need any electron. It can however, donate an electron pair. This species is a Lewis base.
3. Look for the species that can accommodate an electron pair. Such a species has incomplete octet. So this species can accept an electron pair. This species is a Lewis acid.

Solution

1.



2. NH_3 has a lone pair on N-atom. So it is electron pair donor. NH_3 is a Lewis base.
3. Boron in BF_3 has incomplete octet. It has six electrons (3 electron pairs). So it needs

an electron pair to complete its octet. Hence BF_3 is an electron pair accepter or Lewis acid.

Concept Assessment Exercise 9.1

Identify the Lewis acid and the Lewis base in the following examples.

1. $Cl^- + AlCl_3 \longrightarrow [AlCl_4]^-$
2. $H^+ + OH^- \longrightarrow H_2O$

9.3 STRENGTH OF ACIDS AND BASES:

Different Bronsted acids donate proton to different extents. **An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid.** For example, hydrochloric acid is a relatively stronger acid than acetic acid. Also, acetic acid is relatively stronger than water. The ability of an acid to donate proton is called 'strength of acid' or the 'acid strength'. Similarly, the bases also differ in their ability to accept proton. A base which can accept proton to higher degree than another base is a relatively stronger base. Thus ammonia is a relatively stronger base than water because ammonia can accept a proton to a higher degree than water.

9.4 IONISATION CONSTANT OF WATER AND CALCULATION OF pH

Water is a unique compound due to its ability to accept or donate proton under different environments. It has been mentioned earlier that water acts as a Bronsted acid in presence of ammonia, and as a Bronsted base in presence of hydrochloric acid. In fact, Water itself undergoes ionization to a small extent as shown in the following equation:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

This reaction is regarded as auto ionization of water. There is an equilibrium between water molecules (on the left side of the equation) and the hydronium ions and hydroxide ions on the right side of the equation). The equilibrium constant (K) for this equilibrium can be expressed by the following equation.

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since water is a weak electrolyte and solvent, the concentration of water, $[H_2O]$ is in large excess, therefore it remains constant. The above equation may be re-written as:

$$K[H_2O]^2 = [H_3O^+][OH^-]$$

the term $K[H_2O]^2$ is the product of two constants, and is represented by K_w

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

K_w is termed as the Ionic product constant of water. Since $[H_3O^+]$ is the concentration of hydrated protons at equilibrium, the above equation corresponds to:

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

In pure water at 25°C, $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

Whenever $[H^+] = [OH]$,the aqueous solution is found to be neutral, neither acidic nor basic.

$[H^+] = 1.0 \times 10^{-7} M$

$[OH^-] = 1.0 \times 10^{-7} M$

$[H^+][OH^-] = [H^+]^2 = 1.0 \times 10^{-14}$

$[H^+] > [OH^-]$ Acidic solution

$[OH^-] > [H^+]$ Basic solution

It is to be noted that, because K_w is an equilibrium constant, it is temperature dependent thus, at 40 °C $K_w = 3.8 \times 10^{-14}$ which corresponds to

$[H^{+1}] = 1.9 \times 10^{-7}$ M and $[OH^{-1}] = 1.9 \times 10^{-7}$ M as $[H^+] = [OH^-]$

pH

Since the concentration of $[H^+]$ and $[OH^-]$ are usually very small numbers and inconvenient to work with, a more practical measure called pH was proposed and defined as:

$$pH = -\log [H^+]$$

It means that pH of a solution is given by the negative logarithm of the $[H^+]$ concentration (in mol/dm³). However it must be kept in mind that pH being a logarithmic value, does not have any units, the pH concept implies that at 25°C, the different types of solutions will show the following behaviours:

Acidic solution: $[H^+] > 1.0 \times 10^{-7}$ M, $pH < 7.00$

Basic solution: $[H^+] < 1.0 \times 10^{-7}$M, $pH > 7.00$

Neutral solution: $[H^+] = 1.0 \times 10^{-7}$ M, $pH = 7.00$

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

At 25°C, $K_w = 1.0 \times 10^{-14}$

$1.0 \times 10^{-14} = [H^+][OH^-]$

Taking log of both sides

$$\log(1.0 \times 10^{-14}) = \log\left[H^+\right] + \log\left[OH^-\right]$$

$$-14 = -\log[H^+] - \log[OH^-]$$

$$14 = (-\log[H^+]) + (-\log[OH^-])$$

$$14 = pH + pOH$$

Example 9.2

The concentration of $[OH^-]$ ion in a household ammonia solution is 0.005M. Calculate the concentration of $[H^+]$in it.

Solution:

$$[OH^-] = 0.005\,M$$

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

$$1.0 \times 10^{-14} = [H^+] \times 0.005$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.005} = 2.0 \times 10^{-12} M$$

Example 9.3

Calculate the pH of 0.001 M aqueous hydrochloric acid solution.

Solution:

Hydrochloric acid ionizes in water completely therefore,

$$\underset{0.001\,M}{HCl} + H_2O \longrightarrow \underset{0.001\,M}{H_3O^+} + Cl^-$$

$[H_3O^+]$ is in fact the same as $[H^+]$

Therefore $[H^+] = 0.001$ M

$$pH = -\log(0.001)$$

$$= -\log 10^{-3}$$

$$= 3.00$$

Therefore, the pH of 0.001 M aqueous hydrochloric acid is 3.00

Example 9.4

Calculate the pH of 0.062 M NaOH solution.

Solution:

$$\underset{0.062M}{NaOH_{(aq)}} \longrightarrow \underset{0.062M}{Na^+_{(aq)}} + \underset{0.062M}{OH^-_{(aq)}}$$

$$\begin{aligned} pOH &= -\log [OH^-] \\ &= -\log [0.062] \\ &= 1.21 \end{aligned}$$

Now $pH + pOH = 14$

$$\begin{aligned} pH &= 14 - pOH \\ &= 14 - 1.21 \\ &= 12.79 \end{aligned}$$

Concept Assessment Exercise 9.2

What is the pH of a solution containing 1.95g pure H_2SO_4 per dm^3 of solution?

(Ans: pH = 1.4)

9.5 TITRATION:

"It is defined as a method to find the volume of the standard solution required to react completely with known volume of another solution under analysis".

Do You Know?

Sherbet sweets contain a mixture of citric acid, baking soda and icing sugar. When eaten the acid dissolves and reacts with baking soda. The sherbet fizzes on the tongue as carbon dioxide gas is produced by the neutralisation reaction.

Acid-base titrations are conducted using burettes and volumetric pipettes. Generally acid solution is placed in the burette. A fixed volume of base is placed into a conical flask along with a few drops of the suitable acid-base indicator. Acid from the burette is added to the base until the indicator changes colour. This change of colour indicates the end point of titration. In the neutralization of a strong acid with a strong base, phenolphthalein is used as an indicator. It imparts pink colour to the base solution. At the end point, solution just becomes colourless. The molarity of the acid solution under test is determined with the help of the following equation:

$$M_1 V_1 / n_1 = M_2 V_2 / n_2$$

Where M_1 = Molarity of the base

V_1 = Volume of the base taken in flask

M_2 = Molarity of the acid

V_2 = Volume of acid used from the burette

n_1 = No. of moles of base

n_2 = No. of moles of acid

Knowing the five parameters, the sixth can be calculated.

Concept Assessment Exercise 9.3

In a titration it is found that 25 cm^3 of 0.12M NaOH is neutralized with 30cm^3 of HCl of unknown concentration. Calculate concentration and strength of HCl solution.

Solution:

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$$

$$n_1 = 1 \quad n_2 = 1$$

HCl NaOH

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 30}{1} = \frac{0.12 \times 25}{1}$$

$$M_1 = 0.1M$$

Thus Molarity of HCl solution is 0.1M.

Strength of solution = Molarity × Molar mass

Strength of HCl solution = 0.1 × 36.5

= 3.65g dm^{-3}

9.5.1 Selection of Indicators

To perform an acid-base titration, it is necessary to choose the correct indicator. How can you do this? For an acid-base titration, choose an indicator whose pH range is within the limits of the pH change of the reaction. For example,

1. When titrating a strong acid with a strong base, the pH changes rapidly from 3 to 11. The indicator phenolphthalein changes colour from pH 8 to 10. Therefore, phenolphthalein is the best choice for this titration.
2. When titrating a weak acid with a strong base, the pH value changes slightly at the end point. The pH value changes from 6.5 to 10. Which is your choice, phenolphthalein or methyl orange? Since the application range of phenolphthalein is pH 8.3-10, phenolphthalein is the best choice. Methyl orange works below pH 5. For example, oxalic acid versus sodium hydroxide.
3. When titrating a strong acid with a weak base such as HCl vs Na_2CO_3. At the equivalent point, the pH value changes from 3.5 to 7.5. Can you use phenolphthalein in this titration? Methyl orange is the best indicator for this titration. Can you use bromocresol green also?
4. When titrating a weak acid and a weak base, since there is no sharp change in the end point, neither indicator works satisfactorily.

Table 9.1: Indicators and their pH range

Indicator	Acidic Colour	pH Range of Colour Change	Basic Colour
Phenolphthalein	Colourless	8.3-10.0	■
Bromothymol Blue	Yellow	6.0-7.6	Blue
Phenol Red	Yellow	6.8-8.0	■
Methyl Orange	■	3.2-4.4	Yellow

9.6 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. Consider the case of ionization of a general acid HX in water. In this aqueous solution, the established equilibrium may be represented as follows:

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

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 thus,

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

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. 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 is the acid".

The value 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, smaller the value pK_a stronger shall be the acid because smaller pK_a value corresponds to a greater K_a value. In table 8.2 are listed the ionization constants and pK_a values of some common acids in water at 25°C. Which acid is strongest acid? Which acid is weakest acid?

Table 9.2: Ionisation constants and pK_a of Acids

Name of Acid	Formula	Ka	pKa
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 9.5

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

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

Solution:

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

Initial conc.	1.0M	0	0
Eq. conc.	$1.0-x$	x	x
(moles dm^{-3})			

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

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

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

$$1.0 - x = 1.0$$

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

$$x = 0.268\text{M}$$

$$[H^+] = 0.268\text{M}$$

9.7 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 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 referred to as base ionization constant and can be derived in the same way as K_a for acids. Thus:

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

K_b value will be large if 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 K_b value in convenient numbers. Thus, pK_b is defined as the negative logarithm of K_b.

$$pK_b = -\log K_b$$

Table 9.3: 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_3NH_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	$C_6H_5NH_2$	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 a strongest base among all those listed in the table.

9.8 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 on keeping it for a long time.

9.8.1 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 pH more than 7. e.g. $NH_4OH + NH_4Cl$.

9.8.2 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 equal to that of salt and original concentration of acid as equilibrium concentrations, pH of a buffer can be calculated.

The following example explains the calculations associated with buffer solutions.

pH of a buffer can be calculated by using **Henderson's- Hasselbalch equation.**

For Acidic Buffers $$pH = pK_a + \log\frac{[salt]}{[acid]}$$

For Basic Buffers $$pOH = pK_b + \log\frac{[salt]}{[base]}$$

Example 9.6

What is the pH of buffer if concentration of CH_3COOH is 0.1 M and CH_3COONa is 1.0 M. pK_a for CH_3COOH is 4.76?

Solution:

Concentration of CH_3COOH = 0.1 M

Concentration of CH_3COONa = 1.0 M

The formula to determine pH value is

$$pH = pK_a + \log \frac{[salt](i.e. CH_3COONa)}{[acid](i.e. CH_3COOH)}$$

$$pH = 4.76 + \log \left(\text{since } \frac{1.0}{0.1} = \frac{10}{1} \right)$$

$$pH = 4.76 + \log 10 \qquad (\text{as } \log 10 = 1)$$

$$pH = 4.76 + 1.00$$

$$pH = 5.76$$

Concept Assessment Exercise 9.4

Calculate the pH of a buffer solution in which 0.11 Molar CH_3COONa and 0.09 Molar CH_3COOH solutions are present.

K_a for CH_3COOH is 1.8×10^{-5} (Ans: 4.83)

Do You Know?

Biological System	pH Range
Human blood	7.35 to 7.45
Tears	7.40
Stomach	1.65 - 1.75
Milk	6.7 - 6.8
Egg white (protein)	8.0 - 8.1

9.9 SALT HYDROLYSIS

Consider the following observations:

1. Aqueous solution of NH_4Cl turns blue litmus red.
2. Aqueous solution of K_2CO_3 turns red litmus blue.
3. Aqueous solution of NaCl has no action on litmus solutions.

These observations can be explained on the basis of Bronsted-Lowry acid-base theory. When a salt (MX) is dissolved in water, it splits up into its M^+ and X^- ions. These ions may react with water and give following reactions:

$$M^{+} + H-OH_{(l)} \rightleftharpoons MOH_{(aq)} + H^{+}_{(aq)}$$

$$X^{-}_{(aq)} + H-OH_{(l)} \rightleftharpoons HX_{(aq)} + OH^{-}_{(aq)}$$

Since H^+ and OH^- ions are produced in these reactions, the solution of the salt may be acidic or basic. In salts anions are derived from acids and cations from bases. The anions of weak acids are strong conjugate bases. Such anions react with water producing basic solutions.

For example: CH_3COO^-, CN^-, HCO_3^-, CO_3^{2-} etc.

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

$$CN^{-}_{(aq)} + H-OH_{(l)} \rightleftharpoons HCN_{(aq)} + OH^{-}_{(aq)}$$

$$CO_{3\,(aq)}^{2-} + 2H-OH_{(l)} \rightleftharpoons H_2CO_{3\,(aq)} + 2OH^{-}_{(aq)}$$

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

Anions like Cl^-, NO_3^-, SO_4^{2-} are so weak conjugate bases that, they do not react with water. Cations of weak bases are strong conjugate acids. Such cations react with water producing acidic solutions.

For example: Cu^{2+}, Al^{3+}, NH_4^+, etc.

$$Cu^{2+}_{(aq)} + 2H-OH_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H^{+}_{(aq)}$$

$$NH^{+}_{4(aq)} + H-OH_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^{+}_{(aq)}$$

DO YOU KNOW

Hydrolysis is an important process in plants and animals. In living systems, most, biological reactions including ATP hydrolysis, take place during the catalysis of enzymes. The catalytic action of enzymes allows the hydrolysis of fats, proteins and carbohydrates.

Cations like Na^+, K^+, Ca^{2+}, Mg^{2+}, etc. are so weak conjugate acids that they do not react with water.

These reactions are called hydrolysis reactions. **"The chemical reaction of cations and anions of salts with water is called hydrolysis."**

Hydrolysis is different from hydration. In hydrolysis H - OH bond is broken whereas in hydration water molecule adds up to a substance without bond breakage.

There are four types of salts on the basis of their reactivity with water:

1. Salts of strong acids and strong bases do not hydrolyse (pH = 7).

   Examples: $NaCl$, Na_2SO_4, KNO_3 etc.

2. Salts of weak acids and strong bases hydrolyse producing basic solutions (pH>7).

Examples: CH_3COONa, $NaCN$, Na_2S etc.

3. Salts of strong acids and weak bases hydrolyse producing acidic solutions (pH < 7).

   Examples: $CuSO_4$, NH_4Cl, NH_4NO_3 etc.

4. Salts of weak acids and weak bases hydrolyse, but the resulting solution is either neutral, acidic or basic. This depends upon the relative values of K_a and K_b of cations and anions of the salt.

The important aspects of the salt hydrolysis, discussed above, are summarised in Table 9.5.

Table 9.5

Salt Type		Common Example	Ions which impart Hydrolysis	Solution pH (Nature)
Acid	Base			
Strong	Strong	NaCl, K Br	None	= 7.0 (Neutral)
Strong	Weak	NH_4NO_3, NH_4Cl	Cations	< 7.0 (Acidic)
Weak	Strong	NaCN, K_2CO_3	Anions	> 7.0 (Basic)
Weak	Weak	NH_4CN, NH_4NO_2	Anions & Cations	May be equal, smaller or greater than 7.0

9.10 SOLUBILITY PRODUCT AND PRECIPITATION REACTIONS

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

9.10.1 Solubility Product

When an excess of a sparingly soluble ionic compound is mixed with water. Some of it dissolves and the rest of the compound settles to the bottom. A dynamic equilibrium is reached between an insoluble solid compound and its ions in a saturated solution. For example, when it is mixed with water. The following equilibrium occurs.

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

K_c for this equilibrium can be written as

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

DO YOU KNOW

Precipitates are insoluble ionic solid product of a reaction in which certain cations and anions combine in an aqueous solution.

Since CaF_2 is 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 equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balance 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.

9.10.2 Precipitation Reactions

In the previous section, we have considered solids dissolving in solutions. Now we will consider the reverse process i.e. the formation of a solid from solution. **An aqueous reaction that takes place when two or more solution are mixed together, yielding a solid insoluble substance is called precipitation reaction**. In this section we will show how to predict whether a precipitate will form when two solutions are mixed. We will use the term ion product (Q'). It is obtained by substituting initial concentrations instead of equilibrium concentrations in the expression for K_{sp}. For example, ion product expression for solid CaF_2 is given by

$$Q' = [\text{Initial conc. of } Ca^{+2}][\text{Initial conc. of } F^-]^2$$

If we add a solution containing Ca^{2+} ions to a solution containing F^-ions, precipitate may or may not form. To predict whether a precipitation will occur, we compare Q' and K_{sp}. There are two possibilities.

a) If $Q' > K_{sp}$, precipitation occurs and will continue until the concentration satisfy K_{sp}.

b) If $Q' < K_{sp}$, precipitation does not occur.

Example 9.7

The solubility of AgBr is 7.1×10^{-7}M at 25°C. Calculate its K_{sp}.

Solution

7.1×10^{-7}M of dissolved Ag Br produces equal moles of Ag^{+} and Br^{-} ions.

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

$$7.1\times10^{-7}M \qquad 7.1\times10^{-7}M \qquad 7.1\times10^{-7}M$$

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

$$K_{sp} = (7.1\times10^{-7})\,(7.1\times10^{-7})$$

$$K_{sp} = 5.041\times10^{-13}$$

Concept Assessment Exercise 9.5

i. Write K_{SP} expressions for

a) Iron (II)Hydroxide

b) Calcium Sulphate

ii. Lead(II)Sulphate is used as white pigment. What is the solubility of $PbSO_4$?

$K_{sp} = 1.96\text{x}10^{-8}$ at 25 °C **(Ans: 1.4×10^{-4} M)**

iii. Phosphate in natural water often precipitates as insoluble $Ca_3((PO_4)_2$. In Indus river concentration of Ca^{+2} and PO_4^{-3} ions is $1.0\text{x}10^{-9}$M each. Will calcium phosphate precipitate? $K_{sp} = 1.2\text{x}10^{-29}$ at 25°C **(Ans: No)**

9.11 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 $K_a = 7.2\times10^{-4}$, its salt sodium fluoride produces the common ion.

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

$$NaF_{(s)} \overset{H_2O}{\rightleftharpoons} Na^{+}_{(aq)} + F_{(aq)}$$

A strong electrolyte breaks up completely into its ions. HF is a weak electrolyte, it dissociates slightly. NaF being strong electrolyte, completely dissociates in its ions. The common ion F^{-} produced by NaF disturbs this balance. This increases the concentration of F^{-} ions. According to Le Chatelier's principle, the equilibrium shifts to the left to use up some of the F^{-} ions. This reduces HF dissociation. Thus, the dissociation of HF is reduced in the presence of dissolved NaF. This means that the HF concentration increases as a result of the equilibrium change. Similarly, when a highly soluble salt is added to a saturated solution of a less soluble salt containing a common ion. The degree of dissociation of the less soluble salt decreases. Therefore, it reduces its solubility. The term common ion effect is used to describe the behavior of a solution in which two different compounds produce the same ion. **The phenomenon in which the degree of ionization or solubility of an electrolyte is reduced by the addition of a highly soluble electrolyte containing a common ion is called the common ion effect.**

Examples 9.8

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 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 the Le Chatelier's principle K^+ ions will react with ClO_4^- ions to form $KClO_4$. This will suppress, the ionization of $KClO_4$. Thus it will precipitate out.

Examples 9.9

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

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

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

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

Concept Assessment Exercise 9.6

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.

Key Points

- A conjugate acid is a species formed as a result of the acceptance of a proton by a base.
- A conjugate base is the species that remains after donating a proton from an acid.
- A Lewis acid is substance that can accept a pair of electrons to form a coordinate covalent bond.
- A Lewis base is a substance that can donate a pair of electrons to form a coordinate covalent bond.
- NH_3 has a lone pair on N-atom. So it is electron pair donor. NH_3 is a Lewis base.
- An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid.
- It is defined as a method to find the volume of the standard solution required to react completely with known volume of another solution under analysis.
- 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 chemical reaction of cations and anions of salts with water is called hydrolysis.
- The solubility product constant 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.
- An aqueous reaction that takes place when two or more solutions are mixed together, yielding a solid insoluble substance is called precipitation reaction.
- The phenomenon in which the degree of ionization or solubility of an electrolyte is reduced by the addition of a highly soluble electrolyte containing a common ion is called the common ion effect.

References for Further Information

- Michell J. Sienko and Robert A. Plane, Chemistry.
- John W. Hill & Synthia S. Hill, R. D., Chemistry for changing times.
- James N. Lowe, Chemistry, Industry and Environment.
- George M. Bodner and Harry L. Pardue, Chemistry an Experimental Science.

Exercise

1. Choose the correct answer

(ii) Water cannot act as;

(a) Lewis acid (b) Lewis base

(c) Conjugate acid (d) Conjugate base

(iii) pH of 0.01M HCl solution is:

(a) 10^{-2} (b) 10^{+2}

(c) 2.0 (d) 1.0

(iv) An aqueous solution of ammonium chloride is;

(a) Basic
(b) Acidic
(c) Neutral
(d) Amphoteric

(v) An aqueous solution of which compound is basic?

(a) Ammonium nitrate
(b) Calcium chloride
(c) Ammonium acetate
(d) Potassium carbonate

(vi) Which statement about acids is NOT correct? An acid;

(a) Contains hydrogen ions in solution.
(b) Always contains oxygen.
(c) Has a pH of less than 7.
(d) Gives off carbon dioxide from a carbonate.

(vii) If a liquid has a pH of 7;

(a) It must be colourless.
(b) It has boiling point of 100°C.
(c) It must be a solution.
(d) It must be neutral.

(viii) When air is bubbled through pure water, the pH is lowered from 7.0 to 5.6, which gas in the air is responsible for this change?

(a) Argon
(b) Carbon dioxide
(c) Nitrogen
(d) Oxygen.

(ix) If 25cm^3 of 1 mol.dm^{-3} nitric acid is added to 50cm^3 of 0.5 potassium hydroxide solution, what would be the pH of the resulting solution?

(a) 5
(b) 7
(c) 9
(d) 14

(x) If dry citric acid crystals are placed on dry litmus paper it will;

(a) turn yellow
(b) turn green
(c) turn red
(d) remains unchanged

(xi) A base is a substance which will neutralize an acid, which of these substances is not a base?

(a) Aqueous ammonia
(b) Copper oxide
(c) Potassium chloride
(d) Sodium carbonate

(xii) A strong acid;

(a) Is always partially ionized when in solution.

(b) Is always fully ionized when in solution.

(c) Always decomposes carbonates.

(d) Always contains oxygen.

(xiii) Which one of the following oxides dissolves in water to form acidic solution?

(a) MgO (b) Na_2O

(c) SO_2 (d) SiO_2

(xiv) When crystals of copper sulphate are heated, the colour changes from blue to white. This is caused by;

(a) Loss of water only (b) Loss of water and SO_2.

(c) Reaction with CO_2 in the air.

(d) Loss of water, sulphur dioxide and oxygen.

2. Give short answer.

(i) What are conjugate acid-base pairs? Explain with examples.

(ii) Define Lewis acid and Lewis bases. Give one example in each case.

(iii) Write briefly about the ionisation of water.

(iv) Define pH what are the values of pH for acidic, basic and neutral solutions.

(v) What are K_a and pK_a?

(vi) What are K_b and pK_b?

(vii) What is the relationship between K_a and K_b?

(viii) Give two examples of a buffer solution.

(ix) How does temperature impact solubility.

3. Elaborate the ionization equation of water. How does it lead to the ion-product constant of water?

4. What are buffer solutions? Elaborate with suitable examples, their significance in acid-base reactions. Write three common applications of buffer solutions.

5. Write detailed notes on each of the followings:

(a) Conjugate acid base pairs (b) pK_a (c) pK_b

6. What is hydrolysis? Discuss in detail, the behaviour of each of the following salts in their aqueous solutions.

(a) K_2CO_3 (b) NH_4Cl (c) $NaNO_3$

7. Calculate the pH of formic acid-sodium formate buffer solution containing 1.0 mole of each component.
(Ans: 3.7447)

8. When solid $PbCl_2$ is added to pure water at 25°C, the salt dissolves until the concentration of Pb^{2+} reaches 1.6×10^{-2}M. After this concentration is reached, excess solid remains undissolved. What is K_{sp} for this salt.

(Ans: 1.6384×10^{-5})

9. (a) Calculate the H^+ ion concentration of an aqueous solution having pH 10.6.

(Ans: 2.5×10^{-11} moles/dm^3)

(b) An aqueous solution contain 1.0×10^{-9} moles/dm^3 of hydronium ions. Calculate the pOH of this solution

(Ans: 5.0)

10. What is hydrolysis? Write the equations of hydrolysis equilibrium for each of the followings:

(i) K^+ (ii) NH_4^+ (iii) CN^-

11. Compare and contrast the concepts of strong acids and weak acids.
12. Analyse how hydrolysis contribute to the pH of a solution. Provide examples.
13. Discuss the significance of the dissociation constant (K_a) in predicting the behaviour of weak acids.
14. How does the choice of indicators impact the accuracy of titration results.
15. Evaluate the role of water in acid-base chemistry.

Project:

Explore how neutralization reactions are used in daily life. Identify example such as ant acid tablets, baking soda in cooking, or toothpaste. Present your findings in he form of a report.