Unit-08

Acids, Bases and Salts

After reading this unit, the students will be able to:

- Define Bronsted and Lowery concepts for acids and bases. (Remembering)
- Define salts, conjugate acids and conjugate bases. (Remembering)
- Identify conjugate acid-base pairs of Bronsted–Lowery acid and base. (Analyzing)
- Explain ionization constant of water and calculate pH and pOH in aqueous medium using given K_w values. (Applying)
- Use the extent of ionization and the acid dissociation constant, K_a, to distinguish between strong and weak acids. (Applying)
- Use the extent of ionization and the base dissociation constant, K_b, to distinguish between strong and weak bases. (Applying)
- Define a buffer and show with equations how a buffer system works. (Applying)
- Make a buffered solution and explain how such a solution maintains a constant pH, even with the addition of small amounts of strong acid or strong base. (Understanding)
- Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic. (Applying)
- Use concept of hydrolysis to explain why the solution of a salt is not necessarily neutral. (Understanding)
- Define and explain leveling effect. (Understanding)

Teaching 08

Assessment 01

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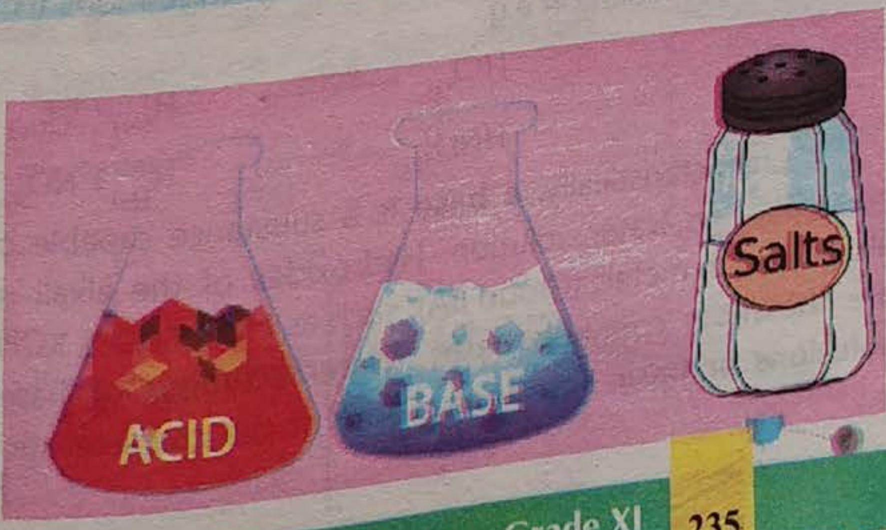


Introduction

Acids and bases play key roles in your bodies, homes and in industrial society. Proteins, enzymes, blood and other components of living matter contain both acids and bases.

Acids were originally identified by their sour taste. Now they are recognized by the colour changes of dyes called indicators and by their reactions with metal oxide, hydroxide and carbonates and also with metals themselves. All of these reactions produce ionic compounds called salts.

Bases were originally identified by their slippery feel. Now they are recognized by their effect on indicators and by the fact that they react with or neutralize acids. If a base dissolves in water, it is called an alkali.

You have already learnt about acids and bases in grade X. In this unit, you will recall the Bronsted- Lowery concept and Lewis concept for acids and bases. You will also study in this unit about conjugate acid - base pairs, strength of acids and bases, pH and pOH, buffer solutions and their applications etc.

8.1 Acidic, Basic and Amphoteric Substances

The word "acid" is derived from the Latin word "acidus", meaning "sour". Some of the characteristic properties commonly associated with ***acids*** are the following:

1. Sour taste
2. The ability to change the colour of litmus, from blue to red
3. The ability to react with,
   - Metals such as zinc and magnesium to produce hydrogen gas
   - Hydroxide bases to produce water and an ionic compound (salt)
   - Carbonates to produce carbon dioxide gas.

These properties are due to the hydrogen ions (H^+) that are released by acids in a water solution e.g.

$$HCl_{(g)} \xrightarrow{H_2O} H^+_{(aq)} + Cl^-_{(aq)}$$

$$HNO_{3(\ell)} \xrightarrow{H_2O} H^+_{(aq)} + NO^-_{3(aq)}$$

Characteristically, a **base** is a substance capable of liberating hydroxide ions (OH^-), in water solution. Hydroxides of the alkali metals (Group IA) and alkaline earth metals (Group IIA), such as LiOH, NaOH, KOH, $Ca(OH)_2$ and $Ba(OH)_2$ are the most common bases. Water solutions of bases are called **alkaline solutions or basic solutions.** Some of the characteristic properties commonly associated with bases are the following:

1. Bitter taste
2. A slippery, soapy feeling
3. The ability to change litmus from red to blue
4. The ability to interact with acids

Their properties are due to the hydroxide ions (OH^-), released by bases in a water solution.

$$NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

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

The process of neutralization of an acid by a base is represented by the reaction of H^+ with OH^- to form water.

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

The substance, which behaves as an acid in basic solution and acts as a base in acidic solution is called amphoteric substance. For example, Water is the most common amphoteric substance. Water may either gain or lose a hydrogen ion (proton) under the appropriate conditions. A substance is said to be amphoteric if it can behave both as an acid and as a base.

For example, water is an amphoteric substance, which behaves as an acid and donates a hydrogen ion (proton) to a base.

$$NH_{3(aq)} + H_2O_{(\ell)} \rightleftharpoons NH^+_{4(aq)} + OH^-_{(aq)}$$

Water accepts a hydrogen ion (proton) and behaves as a base when reacts with hydrochloric acid.

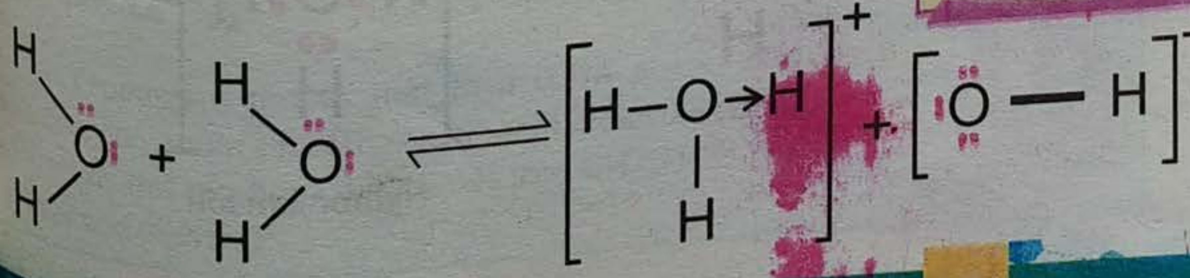
$$HCl_{(aq)} + H_2O_{(\ell)} \rightleftharpoons Cl^-_{(aq)} + H_3O^+_{(aq)}$$

This phenomenon can also be seen clearly in the autoionization (self) of water, which involves the transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion.

Reading Check

Define acid, base and amphoteric substance.

$$\underset{acid(1)}{OH_2} + \underset{base(1)}{H_2O} \rightleftharpoons \underset{acid(2)}{H_3O^+} + \underset{base(2)}{OH^-}$$



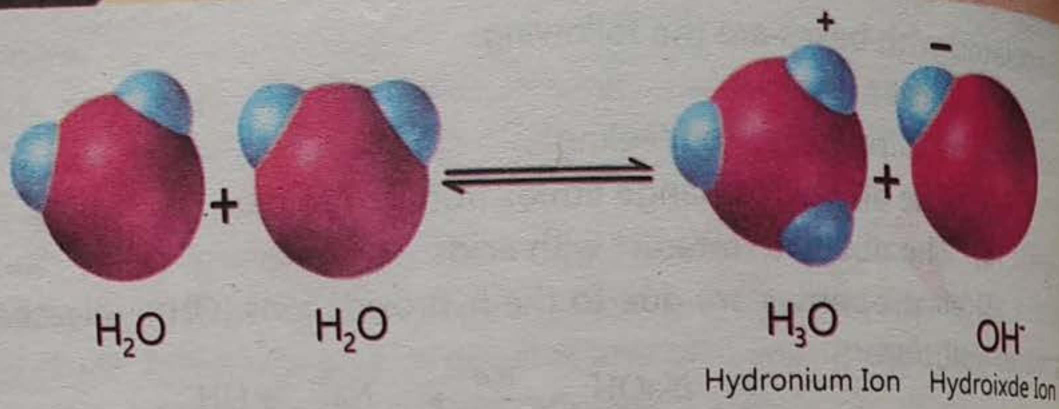


Figure 8.1 Autoionization (self) of Water

8.2 Bronsted – Lowery Definitions of Acids and Bases

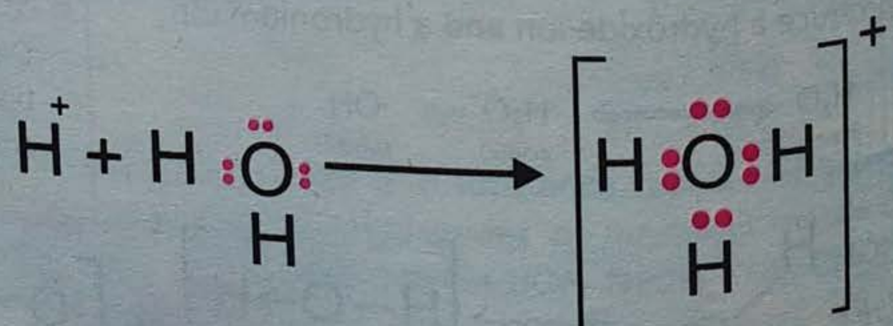
The limitations of the Arrhenius theory of acids and bases are overcome by a more general concept, called the Bronsted-Lowery concept. The Bronsted-Lowery concept defines acids and bases as follows.

An acid is a species (molecule or ion) which donates or tends to donate a proton, whereas, a base is a species (molecule or ion) which accepts or tends to accept a proton.

Tidbit

Hydronium ion

A hydrogen ion (H^+) is nothing more than a proton and does not exist by itself in an aqueous solution. In water H^+ combines with water molecule to form hydrated hydrogen ion (H_3O^+) commonly called a **hydronium ion**. For simplicity it is often used as H^+ instead of H_3O^+ in equations, with the clear understanding that H^+ is always hydrated in solution.



Hydronium Ion

8.2.1 Proton Donors and Acceptors

In acid-base reaction, the acid gives up proton (H^+) and a base accept it i.e. the transfer of a proton from an acid to a base occurs. In other words, a proton donor is an acid and a proton acceptor is a base. For example, hydrochloric acid (HCl) reacts with ammonia (NH_3) to form solid ammonium chloride (NH_4Cl). Hydrochloric acid (HCl) gives up a proton and ammonia accepts it.

$$HCl_{(aq)} + NH_{3(aq)} \rightleftharpoons NH^+_{4(aq)} + Cl^-_{(aq)}$$

Unlike the Arrhenius theory, however, the Bronsted-Lowery theory is not restricted to aqueous solutions.

8.2.2 Relative Strength of Acids and Bases

The Bronsted–Lowery concept considers an acid–base reaction as a proton-transfer reaction. *The stronger acids are those, which lose their protons more easily than other acids. Similarly, the stronger bases are those that hold on to protons more strongly than other bases.*

By comparing various acid–base reactions, you can observe relative strengths of acids and bases in table 8.1.

An acid is strong if it completely ionizes in water. For example, consider the reaction of hydro chloric acid with water.

$$\underset{\text{Acid}}{HCl_{(aq)}} + \underset{\text{base}}{H_2O_{(l)}} \longrightarrow \underset{\text{Base}}{Cl^-_{(aq)}} + \underset{\text{acid}}{H_3O^+_{(aq)}}$$

This reaction occurs in reverse only to an extremely small extent. Because the reaction goes almost completely to the right, so the HCl is a strong acid. The reason that HCl is a strong acid, as it loses its proton readily, more readily than H_3O^+ does. You would say that HCl is a stronger acid than H_3O^+.

As another example, look at the ionization of acetic acid (CH_3COOH), in water.

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

Experiment proves that in a 0.1M acetic acid solution, only about 1% of the acetic acid molecules have ionized by this reaction. This shows that CH_3COOH is a weaker acid than H_3O^+.

Online Check

What is mean by relative strength of acid and bases?

Table 8.1 Relative Strengths of Acids and Bases

	Acid	Conjugate Base	
Strongest Acids	$HClO_4$	ClO_4^-	Weakest Bases
	H_2SO_4	HSO_4^-	
	HI	I^-	
	HBr	Br^-	
	HCl	Cl^-	
	HNO_3	NO_3^-	
	HSO_4^-	SO_4^{2-}	
	H_2SO_3	HSO_3^-	
	H_3PO_4	$H_2PO_4^-$	
	HNO_2	NO_2^-	
	HF	F^-	
	H_2CO_3	HCO_3^-	
	H_2S	HS^-	
	HClO	ClO^-	
	HBrO	BrO^-	
	NH_4^+	NH_3	
	HCN	CN^-	
	HCO_3^-	CO_3^{2-}	
	H_2O_2	HO_2^-	
Weakest Acids	HS^-	S_2^-	Strongest Bases
	H_2O	OH^-	

8.3 Conjugate Acid – Base Pairs

The expansion of the Bronsted – Lowery definition of acids and bases is concept of the conjugate acid-base pair. The dissociation of an acid HA can represented as follows:

$$HA \rightleftharpoons H^+ + A^-$$

For example in case of H_2CO_3

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

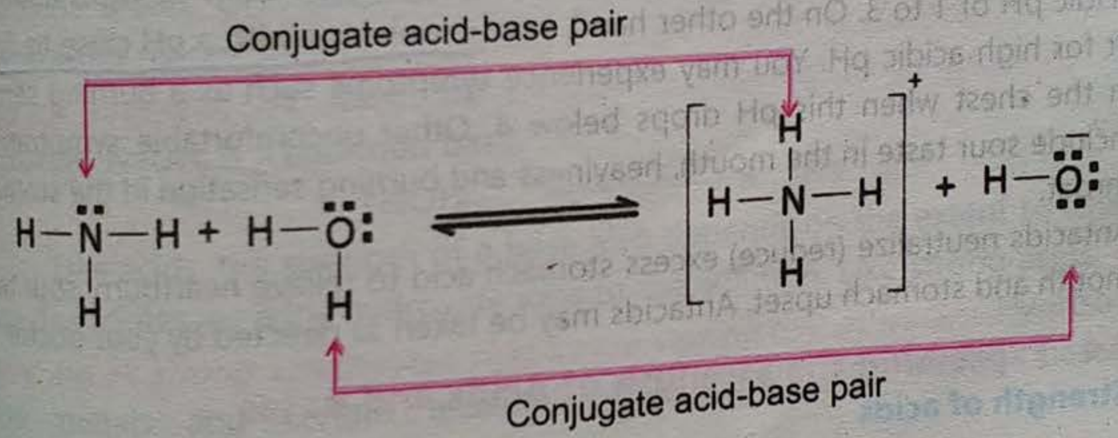
The hydrogen carbonate ion (HCO_3^-) is a base by Bronsted definition is called a conjugate base of carbonic acid. According to Bronsted – Lowry concept, *a reactant and product that differ by a proton (H^+) are called conjugate acid – base pair.* Every acid has a conjugate base and every base has a conjugate acid. Thus, in an acid base reaction, two conjugate pairs are formed.

Conjugate base-acid pair

$$HA_{(aq)} + \bar{B}_{(aq)} \rightleftharpoons \bar{A}_{(aq)} + HB_{(aq)}$$

conjugate acid-base pair

A specie formed from an acid by the loss of a proton is called the conjugate base of that acid and a specie formed from a base by gaining a proton is called the conjugate acid of that base e.g. consider the following reaction.



$$\underset{\text{Base}}{NH_{3(aq)}} + \underset{\text{Acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{Conjugate Acid}}{NH^{+}_{4(aq)}} + \underset{\text{Conjugate Base}}{OH^{-}_{(aq)}}$$

In this case, NH_4^+ is the conjugate acid of the base NH_3, and OH^- is the conjugate base of the acid H_2O. The atom in the Bronsted – Lowery base that accepts an H^+ ion must have a lone pair.

Table 8.2: Some examples of Bronsted-Lowery acids and bases

Acid		Base		Conjugate acid		Conjugate base
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{-2}
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
H_2S	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HS^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
H_2O	+	CO_3^{-2}	$\rightleftharpoons$	HCO_3^-	+	OH^-

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Acidity is a set of symptoms caused by excess production of acid by the gastric glands of the stomach. Your stomach produces acid to digest the food that you eat. This is a regular and natural process. Problem occurs when these cells produce large amount of acid, more than your stomach needs. Gastric juice is a digestive fluid formed in the stomach and is composed of hydrochloric acid (HCl), potassium chloride (KCl) and sodium chloride (NaCl). The pH of gastric acid or hydrochloric acid (HCl) is 1 to 3 in the human stomach. Gastric acid helps to digest and break down food.

Acidity issues arise when there is excess production of this acid. The excess production is due to acidic foods, dehydration, stress etc.

When acidity occurs, the excess acid may move up from your stomach to your esophagus. The lining of your stomach is designed as such to withstand a high acidic pH of 1 to 3. On the other hand, your esophagus with a pH close to 7, is not fit for high acidic pH. You may experience symptoms such as a burning sensation in the chest when this pH drops below 4. Other uncomfortable symptoms may include sour taste in the mouth, heaviness and burning sensation in the stomach or throat.

Antacids neutralize (reduce) excess stomach acid to relieve heartburn, sour taste in mouth and stomach upset. Antacids may be taken as directed by your doctor.

8.4 Expressing the Strength of Acids and Bases

Strength of acids

A strong acid is one that ionizes completely in aqueous solution. Strong acids are strong electrolytes, which for practical purposes, are assumed to ionize completely in water.

Most of the strong acids are inorganic acids such as perchloric acid ($HClO_4$), hydrochloric acid (HCl), nitric acid (HNO_3) and sulphuric acid (H_2SO_4).

$$HClO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + ClO^-_{4(aq)}$$
$$HNO_{3(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + NO^-_{3(aq)}$$
$$HCl_{(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$
$$H_2SO_{4(aq)} + H_2O_{(\ell)} \longrightarrow H_3O^+_{(aq)} + HSO^-_{4(aq)}$$

At equilibrium, solutions of strong acids will not contain any unionized acid molecules.

Weak Acids:

A weak acid is one that ionizes only to a limited extent in water. Acids that are weak electrolytes are known as weak acids. At equilibrium, aqueous solutions of weak acids contain a mixture of unionized acid molecules, H_3O^+ ions, and the conjugate base. Examples of weak acids are hydrofluoric acid (HF), acetic acid (CH_3COOH).

The aqueous solution of a weak acid contains hydronium ions, anions, and dissolved acid molecules. Hydrocyanic acid is an example of a weak electrolyte. In aqueous solution, both the ionization of HCN and the reverse reaction occur simultaneously. Although hydronium and cyanide ions are present in solution, the reverse reaction is favoured. Most of the solution is composed of hydrogen cyanide and water.

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$

Strength of Bases

Most bases are ionic compounds containing metal cations and the hydroxide anion, OH^-. Because these bases are ionic, they dissociate to some extent when placed in solution. *When a base completely dissociates in water to produce aqueous OH^- ions, the solution is referred to as alkaline.* Sodium hydroxide, NaOH, is a common base.

$$NaOH_{(s)} \xrightarrow{H_2O} Na^+_{(aq)} + OH^-_{(aq)}$$

Like acids, the strength of a base also depends on the extent to which the base dissociates, or adds hydroxide ions to the solution. Like strong acids, *strong bases are all strong electrolytes that ionize completely in water.* Hydroxides of alkali metals and certain alkaline earth metals are strong bases e.g. KOH, $Ba(OH)_2$ etc.

Weak Bases: Like weak acids, *a weak base is one that ionizes only to a limited extent in water. Bases that are weak electrolytes are known as weak bases.* Ammonia ionizes in water as follows:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

In this reaction, NH_3 acts as a base by accepting a proton from water to form NH_4^+ and OH^- ions. It is a weak base because only a small amount of the molecules undergo this reaction.

Acids and bases when dissolved in water dissociate into electrically charged ions. The degree of ionization is characteristic of the acids and bases. Strong acids and bases are 100% ionized whereas, weak acids and bases ionize to a certain extent.

The strength of an acid is measured from the tendency to donate a proton and that of a base is the tendency to accept it, it is noted from the acid – base pair that:

A weak acid has a strong conjugate base and vice versa.

A weak base has a strong conjugate acid and vice versa.

For example,

Since acetic acid is a weak acid and its conjugate base (CH_3COO^-) is strong.

$$\underset{\text{weak acid}}{CH_3COOH_{(aq)}} + \underset{\text{Weak base}}{H_2O_{(aq)}} \rightleftharpoons \underset{\text{strong conjugate acid}}{H_3O^+_{(aq)}} + \underset{\text{strong conjugate base}}{CH_3COO^-_{(aq)}}$$

Similarly, ammonia is a weak base and its conjugate acid (NH_4^+) is strong acid.

$$\underset{\text{Weak base}}{NH_{3(aq)}} + \underset{\text{Weak acid}}{H_2O_{(aq)}} \rightleftharpoons \underset{\text{strong conjugate acid}}{NH_4^+{}_{(aq)}} + \underset{\text{strong conjugate base}}{OH^-_{(aq)}}$$

8.4.1 Ionization Equation of Water

Water, as you know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base.

Reading Check

Define strength of acids and bases.

Careful electrical-conductivity experiments have shown that pure water is an extremely weak electrolyte. Water undergoes self-ionization to a small extent, as shown in the model in figure 8.3.

In the self-ionization of water two water molecules produce a hydronium ion and a hydroxide ion by transfer of a proton. This reaction is sometimes also called the *autoionization* of water.

To describe the acid, base properties of water in the Bronsted – Lowery framework, you express its autoionization as follows.

$$\underset{\text{Acid1}}{H_2O} + \underset{\text{Base1}}{H_2O} \rightleftharpoons \underset{\text{Acid2}}{H_3O^+} + \underset{\text{Base2}}{OH^-}$$

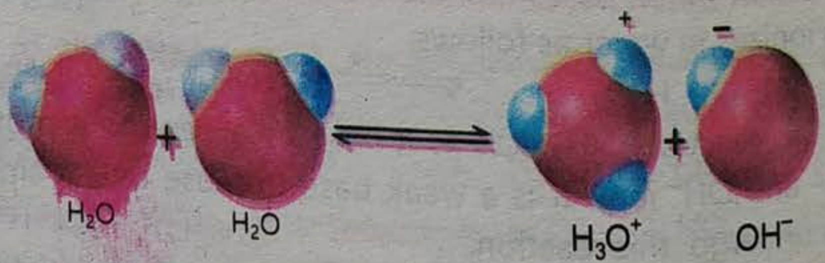


Figure 8.2 Self-Ionization of Water

You can observe the small amount to which the self-ionization of water occurs by noting the small value of its equilibrium constant K_c. Because you can use H^+ (*aq*) and H_3O^+(*aq*) interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed more simply as,

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

Tidbit

$$\underset{Acid1}{H_2O} + \underset{Base1}{H_2O} \rightleftharpoons \underset{acid2}{H_3O^+} + \underset{Base2}{OH^-}$$

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

$$[H_2O]^2 . K_c = [H_3O^+][OH^-]$$

$$K_w = [H_3O^+][OH^-]$$

The equilibrium constant expression is given by the equation.

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad (8.1)$$

Water is in large excess and its concentration remains constant. So on rearranging the equation (8.1), placing $[H_2O]$ with K_c, the ion product $[H^+][OH^-]$ equals a constant.

$$[H_2O].\ K_c = [H^+][OH^-]$$

As

$$[H_2O].\ K_c = K_w$$

So

$$K_w = [H^+][OH^-] \qquad (8.2)$$

Where K_w is called the *ionic product constant (or the dissociation constant) for water, always refers to the autoionization of water, which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.*

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C \qquad (8.3)$$

The concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0\times10^{-7}$ M and $[OH^-] = 1.0\times10^{-7}$ M. Thus, from Equation (8.3), at 25°C,

or

$[H^+] = [OH^-] = 10^{-7}\ mol.dm^{-3}$ in neutral water.

Tidbit

In pure water at 25°C, the value of K_w is 1.0×10^{-14}. Like any equilibrium constant, K_w varies with temperature. At body temperature (37°C), K_w equals to 2.5×10^{-14}.

$$K_w = (1.0 \times 10^{-7})(1.0 \times 10^{-7}) = 1.0 \times 10^{-14}$$

Whether you have pure water or an aqueous solution of dissolved species, the following relation always holds at 25°C,

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \qquad (8.4)$$

Whenever $[H^+] = [OH^-]$ the aqueous solution is said to be neutral. In an acidic solution, there is an excess of H^+ ions and $[H^+] > [OH^-]$. In a basic solution there is an excess of hydroxide ions, so $[H^+] < [OH^-]$. In other words, a solution which contains H^+ ions equal to 10^{-7} M, is said to be neutral. If the hydrogen ions concentration is greater than 10^{-7} M, the solution is said to be acidic whereas, if the concentration is less than 10^{-7} M, the solution is basic.

Self-Assessment

1. Briefly explain amphoteric substance with examples.
2. Give examples of Bronsted-Lowery concept for acids and bases.
3. What is relative strength of acids and bases?
4. What are conjugate acid – base pairs? Give their examples.
5. Define ionization constant of water.

8.4.2 pH, pOH and pK_w

The concentrations of H^+ and OH^- ions in aqueous solutions are very small and, therefore, difficult to work with these small numbers like 10^{-14}. The Danish chemist Soren Sorensen in 1909, proposed a more practical measure of expressing the concentration of H^+ and OH^- ions in terms of pH. The acidity of an aqueous solution depends on the concentration of hydrogen (hydronium) ions. This scale of acidity provides a simple, convenient, numerical way to state the acidity of a solution. Values on the pH scale are obtained by mathematical conversion of H^+ ion concentrations to pH by the expression

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

Where $[H^+]$ = H^+ or H_3O^+ ion concentration in *moles per dm³*. *The pH is defined as the negative logarithm of the H^+ or H_3O^+ concentration in moles per dm³.*

$pH = -\log[H_3O^+]$ or $pH = -\log[H^+]$

A neutral solution at 25°C has a $[H^+]$ of 1×10^{-7} M.

$$pH = -\log[H^+] \qquad (8.5)$$

$$pH = -\log(1 \times 10^{-7})$$

$$pH = -(-7) = 7$$

Therefore, the pH is 7.0.

pH	<	7.00 for an acidic solution	$[H^+] > 1.0 \times 10^{-7}$ M
pH	=	7.00 for a neutral solution	$[H^+] = 1.0 \times 10^{-7}$ M
pH	>	7.00 for a basic solution	$[H^+] < 1.0 \times 10^{-7}$ M

It must be noted that the pH increases as $[H^+]$ decreases.

If you know the pH value of a solution and want to calculate the H^+ ion concentration, then you need to take the antilog of equation (8.5) as follows,

$$[H^+] = 10^{-pH} \qquad (8.6)$$

You can also find simply the pOH, a measure of hydroxide-ion concentration similar to the pH. *The pOH is defined as the negative logarithm of the OH^- concentration in moles per dm^3.*

$$pOH = -\log[OH^-]$$

A solution at 25°C has a $[OH^-]$ of 1×10^{-7} M.

$$pOH = -\log[OH^-] \qquad (8.7)$$

$$pOH = -\log(1 \times 10^{-7})$$

$$pOH = -(-7) = 7$$

Therefore, the pOH is 7.0.

For example, the pH of pure water at 25°C is 7 and is said to be neutral; that is, it is neither acidic nor basic, because the concentrations of H^+ and OH^- are equal. Solutions that contain more H^+ ions than OH^- ions have pH values less than 7, and solutions that contain fewer H^+ ions than OH^- ions have pH values greater than 7.

As you know that $K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

The pK_w is defined as the negative logarithm of K_w. It can be written as,

$$pK_w = -\log K_w$$

Then because, $pK_w = -\log K_w = [H^+][OH^-] = -\log(1.0 \times 10^{-14})$

Taking the logarithm of both sides of the equation,

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

ReadingCheck

Define pH, pOH and pKw.

You will get,

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

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

Hence, $pH + pOH = 14.00$

$$pK_w = 14 \text{ at } 25^\circ C$$

The value of pK_w decreases with increase in temperature.

$$pK_w = pH + pOH = 14.00 \qquad (8.8)$$

Table 8.3 pH Values of Some Common Items

Item	pH
Gastric juice	1 - 2
Lemon juice	2.3
Vinegar	2.8 - 3
Soft drinks	3
Orange juice	3.5 - 3.7
Tomatoes	4 – 4.1
Rainwater	6
Urine	6.0
Milk	6.6
Pure water	7
Human blood	7.3 - 7.4
Baking soda (aqueous)	8.5
Ammonia	11 - 12
Washing soda (aqueous)	12

Table 8.4 Relationship of H_3O^+, OH^-, pH and pOH

	H_3O^+	pH	OH^-	pOH
Basic	1×10^{-14}	14	1×10^{-0}	00
	1×10^{-13}	13	1×10^{-1}	01
	1×10^{-12}	12	1×10^{-2}	02
	1×10^{-11}	11	1×10^{-3}	03
	1×10^{-10}	10	1×10^{-4}	04
	1×10^{-9}	09	1×10^{-5}	05
	1×10^{-8}	08	1×10^{-6}	06
Neutral	1×10^{-7}	07	1×10^{-7}	07
Acidic	1×10^{-6}	06	1×10^{-8}	08
	1×10^{-5}	05	1×10^{-9}	09
	1×10^{-4}	04	1×10^{-10}	10
	1×10^{-3}	03	1×10^{-11}	11
	1×10^{-2}	02	1×10^{-12}	12
	1×10^{-1}	01	1×10^{-13}	13
	1×10^{-0}	00	1×10^{-14}	14

Example 8.1

What is the pH and pOH of 0.001 M HCl solution?

Solution

The concentration of HCl = 0.001 = 10^{-3}

You can write as, $[H^+] = 10^{-3}$

Taking negative log (– log) of both sides , you have,

$$-\log [H^+] = -\log 10^{-3} \qquad \text{as } (\log 10 = 1)$$

As you have,

$-\log [H^+] = pH$, so you can write,

$$pH = -(-3)$$

$$pH = 3$$

Since, you have equation (8.8),

$$pH + pOH = 14$$

or

$$pOH = 14 - pH$$

$$pOH = 14 - 3$$

$$pOH = 11$$

Example 8.2

Determine the pH of 0.15M NaOH solution.

Solution

The concentration of NaOH = 0.15 = 1.5×10^{-1}

You can write as, $[OH^-] = 1.5 \times 10^{-1}$

Taking negative log (–log) of both sides , you have,

$$-\log [OH^-] = -\log 1.5 \times 10^{-1}$$

$$-\log[OH^-] = -(0.2 - 1)$$

$$-\log[OH^-] = -(-0.8)$$

$$-\log[OH^-] = 0.8$$

Or you can write, $pOH = 0.8$

as you have,

$$pH + pOH = 14$$

or

$$pH = 14 - pOH$$

$$= 14 - 0.8$$

Example 8.3

Calculate the $[H^+]$ and $[OH^-]$ ions concentration of a solution, which has a pH of 4.

Solution

pH of solution = 4

$[H^+] = ?$, $[OH^-] = ?$

Since you have the equation (8.6) ,

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

Putting the values, you get,

$$[H^+] = 10^{-4}$$

As you have,

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

Putting the values, you get,

$$[OH^-] = \frac{10^{-14}}{[10^{-4}]}$$

$$[OH^-] = 10^{-14+4} = 10^{-10}$$

Practice Problem 8.1

Calculate the pH of 0.002 M hydrochloric acid (HCl) solution.

Practice Problem 8.2

Find the pH of 0.082 M NaOH solution.

8.4.3 Acid Ionization Constant, K_a and pK_a

Consider a weak monoprotic acid, HA. Its ionization in water is represented by

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

The equilibrium expression fo. this ionization is

$$K_c = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \qquad (8.9)$$

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

Where for acid is, $K_c \cdot [H_2O] = K_a$, so you can write the above equation as,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad (8.10)$$

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

Where K_a, the acid ionization or dissociation constant. It is the equilibrium constant for the ionization of an acid. At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of K_a. It is the ratio of product of concentrations of dissociated ions to the undissociated acid molecules in aqueous solution. It represents the extent to which an acid is dissociated. The larger the value of K_a, the stronger will be the acid, that is, the greater will be the concentration of H^+ ions at equilibrium due to its ionization. Keep in mind, however, that only weak acids have K_a values associated with them.

A negative logarithm of K_a is called pK_a. Since it is the negative logarithm, hence greater the value of pK_a, weaker would be the acid.

$pK_a = -\log K_a$ (8.11)

Table 8.5 lists a number of weak acids and their K_a values at 25°C in order of decreasing acid strength. Although all these acids are weak, within the group there is great variation in their strengths.

Table 8.5 Ionization Constants of Some Weak Acids at 25°C

Substance	Formula	Ka
Acetic acid	CH_3COOH	1.7×10^{-5}
Benzoic acid	C_6H_5COOH	6.3×10^{-5}
Boric acid	H_3BO_3	5.9×10^{-10}
Carbonic acid	H_2CO_3	4.3×10^{-7}
Cyanic acid	$HOCN$	3.5×10^{-4}
Formic acid	$HCOOH$	1.7×10^{-4}
Hydrocyanic acid	HCN	4.9×10^{-10}
Hydrofluoric acid	HF	6.8×10^{-4}
Hydrogen sulphide	H_2S	8.9×10^{-8}
Hypochlorus acid	$HOCl$	3.5×10^{-8}
Nitrous acid	HNO_2	4.5×10^{-4}
Oxalic acid	$(COOH)_2$	5.6×10^{-2}
Phosphoric acid	H_3PO_4	6.9×10^{-3}
Phosphorus acid	H_3PO_3	1.6×10^{-2}
Propionic acid	$C_3H_6O_2$	1.4×10^{-5}
Sulphurous acid	H_2SO_3	1.3×10^{-2}

8.4.4 Leveling Effect

Strong acids, such as HCl, HBr, and HI, all show nearly same strength in water. The water molecule is such a strong base compared to the conjugate bases Cl^-, Br^-, and I^- that ionization of these strong acids is essentially complete in aqueous solutions. *The phenomenon by which the strength of different strong acids having close values of pK_a is levelled (equalized) by a definite solvent is called leveling effect.* The acid strength depends upon the solvent chosen.

They appear to have nearly equal strengths because their strengths are due to that of hydronium ion (H_3O^+). All the acids, which are completely dissociated in aqueous solution, are expressed by H_3O^+ ion. It is not possible to find the order of increasing strengths of these acids because they are completely ionized.

In solvents less basic than water, you will be able to find that HCl, HBr, and HI differs clearly in their tendency to give up a proton to the solvent. For example, when dissolved in or acetic acid ethanol (a weaker base than water), the extent of ionization increases in the order HCl < HBr < HI, and so HI is demonstrated to be the strongest of these acids.

The same effect is noticed in the case of solutions of bases. Water also exerts a leveling effect on the strengths of strong bases. For example, the oxide ion, O^{-2}, and the amide ion, NH_2^{-1} are such strong bases that they react completely with water. When Na_2O and $NaNH_2$ are dissolved in water, they give following reactions.

$$O^{-2}_{(aq)} + H_2O_{(\ell)} \longrightarrow OH^-_{(aq)} + OH^-_{(aq)}$$

$$NH^{-1}_{2(aq)} + H_2O_{(\ell)} \longrightarrow NH_{3(aq)} + OH^-_{(aq)}$$

The reaction goes to competition and thus, O^{-2} and NH_2^- appear to have the same basic strength in water; they both give a 100% yield of hydroxide ion. The basic strength of O^{-2} and NH_2^{-1} is leveled to the strength of OH^- ions and they behave as equally strong bases in aqueous solution.

The approximate values of pK_a of some of the acids are given in table 8.6

Table 8.6 pK_a Values (Approximately) of Some Acids In Water

Acids	pK_a	Acids	pK_a
$HClO_4$	– 10	$(COOH)_2$	1.3
HI	– 10	H_2SO_3	1.8
HBr	– 9	CH_3COOH	4.7
HCl	–7	H_2CO_3	6.4
H_2SO_4	–3 -2	H_2S	7.0
HNO_3	–3 -3	NH_4^+	9.3
$HClO_3$	–3	HCN	9.4

8.4.5 Base Ionization Constant, K_b and pK_b

The ionization of weak bases is treated in the same way as the ionization of weak acids.

Consider a weak Bronsted base, A^-. Its ionization in water is represented by

$$A^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

The equilibrium expression for this ionization is

$$K_c = \frac{[HA][OH^-]}{[H_2O][A^-]} \qquad (8.12)$$

$$K_c.[H_2O] = \frac{[HA][OH^-]}{[A^-]}$$

Where for base is, $K_c.[H_2O] = K_b$, so you can write the above equation as,

$$K_b = \frac{[HA][OH^-]}{[A^-]} \qquad (8.13)$$

Where K_b, the *base ionization or dissociation constant. It is the equilibrium constant for the ionization of base.* At a given temperature, the strength of the Bronsted base, A^- is measured quantitatively by the magnitude of K_b. The larger the value of K_b, the stronger will be the base, that is, the greater the concentration of OH^- ions at equilibrium due to its ionization. A negative logarithm of K_b is pK_b. Keep in mind, however, that only weak bases have K_b values associated with them.

$$pK_b = -\log K_b \qquad (8.14)$$

Table 8.7 Ionization Constants of Some Weak Bases at 25°C

Substance	Formula	K_b
Ammonia	NH_3	4 1.8×10^{-5}
Aniline	$C_6H_5NH_2$	8 4.2×10^{-10}
Dimethylamine	$(CH_3)_2NH$	1 5.1×10^{-4}
Ethylamine	$C_2H_5NH_2$	2 4.7×10^{-4}
Hydrazine	N_2H_4	5 1.7×10^{-6}
Hydroxylamine	NH_2OH	6 1.1×10^{-8}
Methylamine	CH_3NH_2	3 4.4×10^{-4}
Pyridine	C_5H_5N	7 1.4×10^{-9}
Urea	NH_2CONH_2	9 1.5×10^{-14}

8.4.6 Relationship of K_a and K_b

According to Bronsted – Lowery concept when a weak acid or a weak base is dissolved in water, a conjugate acid-base pair is produced. An important relationship between the acid ionization constant, K_a and the ionization constant of its conjugate base, K_b, can be derived as follows, using the general equation of an acid as an example is,

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

You have an equation for K_a, given in equation (8.10) previously,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad (8.10)$$

The general equation of base as an example is,

$$A^-_{(aq)} + H_2O_{(\ell)} \rightleftharpoons HA_{(aq)} + OH^-_{(aq)}$$

You have an equation (8.13) for K_b,

$$K_b = \frac{[HA][OH^-]}{[A^-]} \qquad (8.13)$$

Multiplying the expression of K_a with that of K_b

$$K_a \times K_b = \frac{[H_3O][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

On simplification you get,

$$K_a \times K_b = [H_3O^+] \times [OH^-] = [H^+][OH^-]$$

$$K_a \times K_b = [H^+][OH^-]$$

As you know that, $[H^+][OH^-] = K_w$

$$K_a \times K_b = K_w \text{ ------------- } (8.14) \qquad (K_w = 1.0 \times 10^{-14})$$

You can write, the above equation (8.14), as

$$K_a = \frac{K_w}{K_b}$$

This enables you to draw an important conclusion: The stronger the acid (the larger K_a), the weaker its conjugate base (the smaller K_b), and vice versa. As K_w being constant, so, you can write as,

$$K_a \propto \frac{1}{K_b}$$

Using the equation $K_a \times K_b = K_w$ (8.14)

Taking negative logarithm (– log) of the equation (8.14),

$(-\log K_a) + (-\log K_b) = -\log K_w$

So you can write,

$$pK_a + pK_b = 14 \quad (8.15)$$

$$pK_a = 14 - pK_b$$

Knowing the pK_a value of an acid, you can find the pK_b of its conjugate base and vice versa.

Example 8.4

Acetic acid (CH_3COOH) has a pK_a value of 4.7 at 25°C. What is the pK_b value of its cojuagte base, CH_3COO^-?

Solution

The value of $pK_a = 4.7$

Value of $pK_b = ?$

As

$pK_a + pK_b = 14$

or

$pK_b = 14 - pK_a$

or

$pK_b = 14 - 4.7$

$pK_b = 9.3$

8.5 Lewis Definitions of Acids and Bases

A more general and broader concept of acids and bases was introduced by Gilbert N. Lewis. According to this concept, *a Lewis acid is any specie (molecule or ion) that can form a covalent bond by accepting an electron pair from another species; a Lewis base is a specie that can form a covalent bond by donating an electron pair to any other specie.*

The Lewis acid

Those compounds which are electron deficient or which have less than eight electrons (octet) in valence shell behave as Lewis acids, e.g.

Lewis acid Lewis base

Positive ions (cations) are often considered as acids.

$$\underset{\text{Acid}}{Ag^{+}} + \underset{\text{Base}}{2\ddot{N}H_3} \longrightarrow [Ag(NH_3)_2]^{+}$$

Lewis base

Molecules containing an atom with lone pair of electrons are bases. For example, $\ddot{N}H_3$ with a lone pair of electron is base.

Negative ions (anions) are Lewis bases e.g.

$$\underset{\text{Base}}{OH^{-}} + \underset{\text{Acid}}{H_3O^{+}} \rightleftharpoons H_2O + H_2O$$

$$\underset{\text{Base}}{Cl^{-}} + \underset{\text{Acid}}{H_3O^{+}} \rightleftharpoons HCl + H_2O$$

For example, in the protonation of ammonia, NH_3 acts as a *Lewis base* because it donates a pair of electrons to the proton H^+, which acts as a *Lewis acid* by accepting the pair of electrons.

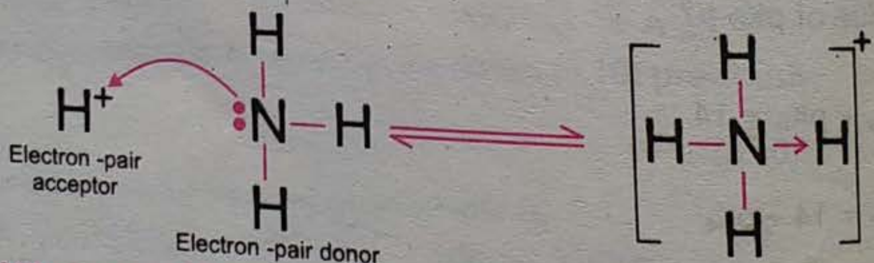
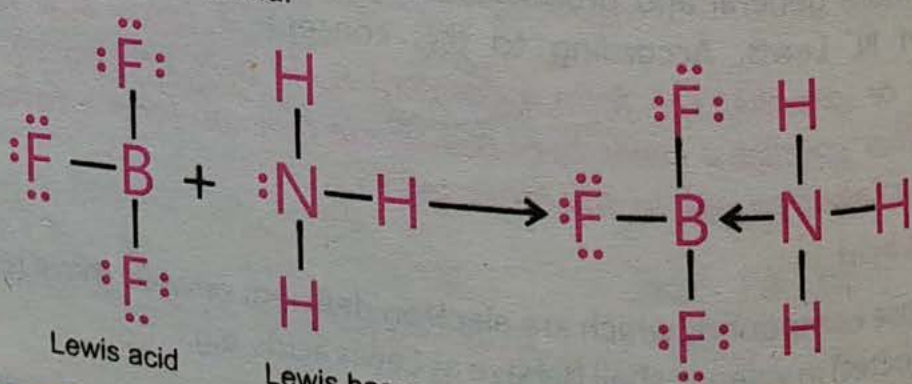


Figure 8.4 The proton H^+, acts as a Lewis Acid by accepting the pair of electrons

The significance of the Lewis concept is that it is much more general than other definitions; it includes many acid-base reactions that do not involve Bronsted acids and bases. Consider, for example, the reaction between boron trifluoride (BF_3) and ammonia.



Lewis acid Lewis base

A Lewis acid-base reaction, therefore, is one that involves the donation of a pair of electrons from one specie to another. Such a reaction does not produce a salt and water and is not restricted to any particular solvent.

Table 8.8 Summary of Three Concepts of Acids and Bases

Concept	Definition of acid	Definition of base
Arrhenius	H^+ producer	OH^- producer
Bronsted – Lowery	H^+ donor	H^+ acceptor
Lewis	Electron pair acceptor	Electron pair donor

Self-Assessment

1. What is pK_a and pK_b?
2. What is meant by leveling effect?
3. What is K_w?
4. What are Lewis acids, explain it with examples?
5. What is the significance of Lewis concept? Explain it with suitable examples.
6. How the sum of pK_a and pK_b is equal to 14.

SOCIETY, TECHNOLOGY AND SCIENCE

Milk is mixture of different components. The major components of milk are protein, fat and water. When you talk about the curdling of milk, you are mainly concerned with one specific milk protein called casein.

Casein groupings are spread evenly throughout the milk. Normally, casein groupings float around in the milk without bonding to anything. These groupings have a negative charge, which makes them repel other groupings of casein and keeps the casein evenly dispersed in the milk. Casein has a tendency to get precipitated and combined.

When lemon juice is added, it increases milk's acidity because lemon contains citric acid. When milk becomes acidic, the negative charge, which keeps the casein separate, is neutralized. Now instead of pushing each other apart, the casein starts to clump together. Eventually large enough clumps are formed that you can actually see the separation, and then you have curdled milk.

8.6 Buffer Solutions and their Applications

Pure water has a pH value equal to 7, but even the purest form of water cannot retain this value of pH for long time. The reason is that carbon dioxide in the air dissolve in water and gives it a slight acidic character or the silicates from the glass may change its pH.

A solution, which resists changes in pH when a small amount of a stro acid or a strong base is added to it, is called a buffer solution. In other words, can say that a buffer is one which maintains its pH fairly constant even upon addition of small amounts of acid or base.

Buffers are very important to chemical and biological systems. The pH the human body varies greatly from one fluid to another; for example, the pH blood is about 7.4, whereas the gastric juice in our stomachs has a pH of abo 1.5. Buffers in most cases maintain these pH values, which are crucial for t proper functioning of enzymes and the balance of osmotic pressure.

A ***buffer solution*** is usually prepared from

- A weak acid and its salt with a strong base. These are called **Acidi buffers,** such as CH_3COOH and CH_3COONa; such buffers are acidic with p less than 7.
- A weak base and its salt with a strong acid. These are called **Basi buffers,** such as NH_4OH and NH_4Cl; such solutions have a pH more than 7.

Buffer Action

The resistance offered by a buffer solution to change in pH on t addition of acid or base is called a buffer action. The buffer action for acidic a basic buffers is explained as under.

i. Weak Acid and its Salt Buffers

A simple buffer solution can be prepared by adding comparable amou of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa) to water. A soluti containing these two substances has the ability to neutralize the added acid base.

The pH of the buffer is governed by the equilibrium

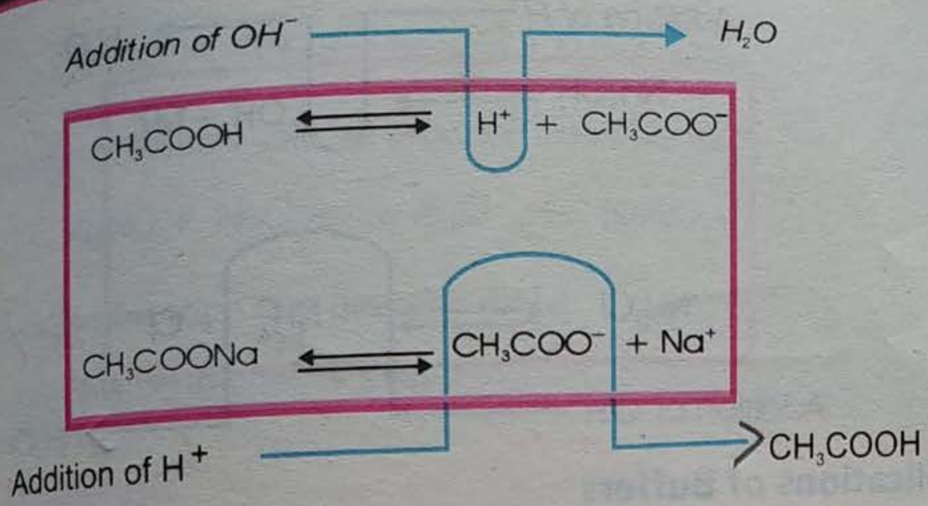
$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)} \quad (8.16)$$

Sodium acetate, a strong electrolyte, dissociates greatly in water:

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

a. Addition of Strong Base

When a small amount of strong base like, NaOH is added, it will incre the concentration of OH^-. The excess of OH^- combine with the H^+ of acetic a to form water molecules. As a result, the equilibrium (8.16) shifts to the right produce more H^+ ions till all the excess OH^- ions are neutralized and the origi pH of the buffer is restored. More acetic acid is ionized to recover the deficie of H^+ ions. Therefore, the pH of the buffer solution will not change.



Addition of Strong Acid

When a strong acid is added, H^+ ion of the acid reacts with the acetate ion f the buffer.

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

Both of these reactions go to completion. Hence, the added OH^- and H^+ ons are removed and the pH of the buffer solution remains constant.

Weak Base and its Salt Buffers

The example of this buffer is, *NH_4Cl and NH_4OH*. Its resistance to change n pH can also be explained on the same lines as that of an acid buffer.

Addition of Strong Acid

When a small amount of strong acid like HCl is added to the buffer; the H^+ ons combine with OH^- ions of the NH_4OH to form water molecules.

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

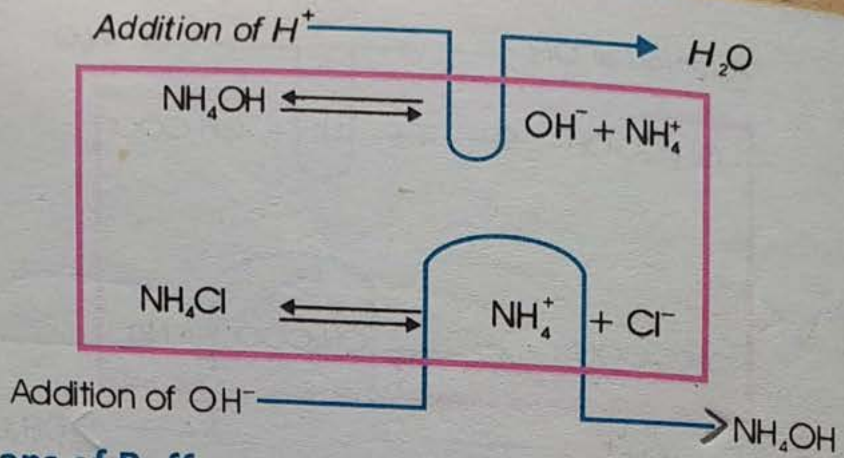
The equilibrium is shifted to the right till all the additional H^+ ions are neutralized and the original buffer pH is restored.

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

Addition of Strong Base

When small amount of strong base such as, NaOH is added to the buffer solution, concentration of the OH^- increases. The OH^- combines with excess of NH_4^+ ions to form the NH_4OH. Thus, the pH of the buffer remains constant.

$$NH_4^+{}_{(aq)} + OH^-_{(aq)} \rightleftharpoons NH_4OH_{(aq)}$$



Applications of Buffers

i. The use of buffers is important in some industrial processes, which wou be interrupted by large change in pH. Examples are manufacture leather, photographic materials and dyes.

ii. In bacteriological research, culture media are generally buffered maintain a constant pH required for the growth of the bacteria bei studied.

iii. Buffer is important in biological systems because biological reactions both plants and animals are often very sensitive to pH changes. Huma blood is buffered to a pH of 7.4 by means of bicarbonates, phosphat and complex protein systems.

iv. Protein studies must be performed in buffered media because th magnitude and kind of electrical charge carried by protein molecul depend on the pH.

Reading Check

What is buffer solution?

Tidbit

Salt

A salt is formed when a base is neutralized by an acid. A salt consists of metallic and acidic radical. Examples are NaCl, $NaNO_3$, Na_2SO_4, KCl etc

Salt are prepared by the following methods.

Neutralization of a base by an acid.

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(aq)}$$

Reaction of an acid with a reactive metal

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Reaction of an acid with carbonate (CO_3^{-2}) or bicarbonate (HCO_3^-)

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

Reaction of soluble salts to produce insoluble salts

$$AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$$

Direct combination of a gas with metal

$$2Na + Cl_2 \longrightarrow 2NaCl$$

8.7 Salt Hydrolysis

A salt is an ionic compound formed by the reaction between an acid and a base. Some salts are strong electrolytes that completely dissociate in water and in some cases partially dissociate in water.

The term salt hydrolysis describes the reaction of an anion or a cation or both the ions of a salt with water to produce acidic,basic or neutral solutions.

Hydrolysis is defined as, the reaction of an anion or cation with water accompanied by cleavage of H–O–H bond.

When a salt is dissolved in water, it is dissociated into positive and negative ions. These ions separately react with water by breaking the H–OH bond. As a result,an acidic or basic solution is formed depending upon the nature of the dissolved salt.

It may be noted that in **anionic hydrolysis** the solution becomes slightly basic due to the generation of excess OH^- ions.

$$\bar{A} + H-O-H \rightleftharpoons HA + \bar{OH}$$

In **cationic hydrolysis**, there is excess of H^+ ions, which makes the solution slightly acidic.

$$\overset{+}{B} + H-O-H \rightleftharpoons BOH + \overset{+}{H}$$

The different salts may be classified into the following types according their hydrolytic behaviour:

(1) Salts of weak acids and strong bases
(2) Salts of weak bases and strong acids
(3) Salts of weak acids and weak bases
(4) Salts of strong acids and strong bases.

1. Salts of Weak Acids and Strong Bases

pH => 7

When a salt of weak acid (CH_3COOH) and Strong base (NaOH), for example, sodium acetate (CH_3COONa) is dissolved in water. It ionizes in aqueous solution, into CH_3COO^- and Na^+.

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

Being the conjugate base of a weak acid, CH_3COOH, CH_3COO^- is a relatively strong base. Thus, CH_3COO^- accepts H^+ ion from water and undergoes hydrolysis.

strong C.B

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

The resulting solution is slightly basic due to excess OH^- ions present.

2. Salts of Weak Bases and Strong Acids

pH =< 7

When a salt of weak base (NH_4OH) and strong acid (HCl), for example, ammonium chloride (NH_4Cl) is dissolved in water. In aqueous solution, it ionizes into NH_4^+ and Cl^-.

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

NH_4^+ is a Bronsted conjugate acid of the weak base NH_4OH. Therefore it is a relatively strong acid. It accepts OH^- ion from water (H_2O) and forms the unionized NH_4OH and H^+ ion.

Strong C.A

$$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$

The accumulation of H^+ ions in solution makes it acidic.

Tidbit

Hydration and Hydrolysis

In hydrolysis H–OH bond is broken down; while in hydration water molecules combine to a substance without H–OH bond breaking and become part of that substance molecule.

3. Salts of Weak Acids and Weak Bases

When a salt of weak acid (CH_3COOH) and weak base (NH_4OH), for example, ammonium acetate (CH_3COONH_4) is dissolved in water. It ionizes into CH_3COO^- and NH_4^+. Since the acid and the base are both weak, their conjugate base (CH_3COO^-) and conjugate acid (NH_4^+) are relatively strong. They accept H^+ and OH^- ions, respectively, from water and undergo considerable hydrolysis.

$$CH_3COO^- + H_2O \longrightarrow CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$$

The overall hydrolysis may be represented as,

$$CH_3COO^- + NH_4^+ + H_2O \longrightarrow CH_3COOH + NH_4OH$$

The pH of the resulting solution will depend on the relative extent of anionic hydrolysis and cationic hydrolysis. The solution of such salt may be acidic, basic or neutral depending upon the K_a and K_b values of acid and base, respectively. If both the ions react to the same extent (as shown for CH_3COONH_4), $[OH^-] = [H^+]$. Then solution is neutral.

4. Salts of Strong Acids and Strong Bases

The salts of strong acid (HCl) and strong base (NaOH) such as, NaCl, does not show hydrolysis. When NaCl is added into water, NaCl dissociates in water to give Na^+ and Cl^- ions.

Since HCl is a strong acid, Cl^- is very weak conjugate base of HCl, Cl^- is unable to accept a proton (H^+) from an acid, particularly water. That is why Cl^- does not hydrolyse. It cannot generate OH^- ions as follows.

$$Cl^- + H_2O \not\longrightarrow HCl + OH^-$$

Similarly, in NaOH case, Na^+ is not hydrolyzed because it is conjugate acid of strong base NaOH. Thus, the pH of sodium chloride solution remains unaffected and neutral.

Self-Assessment

1. What is buffer action also write its application.
2. What is hydrolysis? Explain why aqueous solutions of some salts are acidic or basic.
3. Explain why the solution of a salt is not necessarily neutral.

KEY POINTS

- Brontsed acid is a species (molecule or ion) which donates or tends to don a proton.
- Brontsed base is a species (molecule or ion) which accepts or tends to acc a proton.
- Stronger Brontsed acids are those that lose their protons more easily th other acids.
- Stronger Brontsed bases are those that hold on to protons more stron than other bases.
- A species formed from an acid by the loss of a proton is called the conjug base of that acid and a specie formed from a base by gaining a proton called the conjugate acid of that base.
- A strong acid is one that ionizes completely in aqueous solution.
- A weak acid is one that ionizes only to a limited extent in water.
- Acid-base reaction involves the transfer of a proton from an acid to a base weak acid has a strong conjugate base while a weak base has always a stro conjugate acid.
- Ionic product of water, K_w is a constant quantity equal to 1×10^{-14} at 25°C.
$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$
- When a base completely dissociates in water to yield aqueous OH^- ions, th solution is referred as alkaline.
- Strong bases are all strong electrolytes that ionize completely in water.
- A weak base is one that ionizes only to a limited extent in water.
- In the self-ionization of water, two water molecules produce a hydronium ic and a hydroxide ion by transfer of a proton. This is called the autoionizatio of water.
- Water is an amphoteric substance: it behaves both as an acid and a base.
- pH is the negative logarithm of the H^+ or H_3O^+ concentration in moles p dm^3, smaller the value of pH, greater is the acidity.
- The pOH is defined as the negative logarithm of the OH^- concentration i moles per dm^3.
- K_a, the acid ionization constant, is the equilibrium constant for the ionizati of an acid.

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

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

- A strong acid has a very large K_a value.
- pK_a is the negative logarithm of K_a. So greater the value of pK_a, lower is the strength of an acid.
- Base – ionization constant, K_b, is the dissociation constant of a base and pK_b is the negative logarithm of K_b. If a substance has greater value of dissociation constant K_b, and smaller pK_b value then it will be strong base.
- K_b, the base ionization constant, is the equilibrium constant for the ionization of base.
- A Lewis acid is a species that can accept an electron pair from another species.
- A Lewis base is a species that can donate an electron pair to another species.
- Lewis acid – base reaction involves the exchange of a proton from an acid to a base. A weak acid has a strong conjugate base while a weak base has always a strong conjugate acid.
- A solution, which resists a change in pH when a small amount of a strong acid or a strong base is added to it, is called a buffer solution.
- Acid buffer contains a weak acid and its salt with a strong base.
- Basic buffer contains a weak base and its salt with a strong acid.
- Buffer action is the resistance offered by a buffer solution to change in pH on the addition of small amount of an acid or base.
- Hydrolysis is the reaction of an anion or cation of a salt with water accompanied by cleavage of H–O–H bond.

EXERCISE

Choose the correct option.

1. Which one is the example of buffer
   a. HCl/ NaCl b. NaOH/ H_2CO_3
   c. NH_4OH/NH_4Cl d. NaOH/ NaCl
2. Conjugate acid – base pair differs by
   a. A proton b. A proton pair
   c. An electron d. An electron pair
3. 1 M solution of $Ca(OH)_2$ is mixed with 1M solution of HCl. The product solution is
   a. Acidic b. Basic c. Neutral d. Amphoteric
4. Cl^- is the conjugate base of
   c. $AlCl_3$ b. NaCl c. HCl d. KCl
5. pH of an aqueous solution is 9. Its pOH is
   a. 11 b. 9 c. 7 d. 5
6. Salt of a weak base and strong acid has a pH, approximately
   a. 8 b. 6 c. 7 d. 9
7. The unit of K_w is,
   a. Mole $.dm^{-3}$ b. $Mole^{-2}$ $.dm^{-6}$
   c. $Mole^2$ $.dm^{-6}$ d. $Mole^2$ $.dm^{-3}$
8. Very large Ka value means that the substance is a
   a. Strong acid b. Weak acid
   c. Weak base d. Strong base
9. In following halogen acids which one is the strongest acid
   a. HF b. HCl c. HBr d. HI
10. Which one of following solution have zero pH
    a. 1M HCl b. 0.5M H_2SO_4
    c. 0.1M HNO_3 d. 1M CH_3COOH
11. Which one is not true for acids
    a. Liberate H^+ b. Accepts electrons
    c. Have high pH d. Turn blue litmus red
12. 10^{-3} moles of HNO_3 is dissolved $/dm^3$. Its pH is
    a. –3 b. 5 c. 3 d. 1

13. A solution with a pK_a value of 9, suggest that it is a
    a. Strong acid b. Weak acid
    c. Weak base d. Strong base
14. Cl^- is a / an
    a. Acid b. base c. Amphoteric d. None
15. An acidic buffer solution can be prepared by mixing
    a. Weak acid and its salt with strong base
    b. Strong acid and its salt with weak base
    c. Weak base and its salt with strong acid
    d. Strong base and its salt with weak acid

Short Questions

1. What information would you use to support the view that water can act either as a weak acid or as a weak base?
2. Explain that why the sum of pK_a and pK_b is always equal to 14.
3. Explain why the conjugate base of a strong acid is a weak base and the conjugate acid of a strong base is a weak acid.
4. Justify your answer with equations that CH_3COONa gives a basic solution while NH_4Cl an acidic solution in water.
5. Why do you call $AlCl_3$ and BF_3 as Lewis acids, Cl^- and NH_3 as Lewis bases?

Numerical Questions

1. What is the pH of 0.0001M $Ca(OH)_2$ solution. (Ans. pH = 10.3)
2. What is $[H^+]$ and $[OH^-]$ ions concentration of solution, which has a pH of 4.87? (Ans. $[H^+] = 1.35\times 10^{-5}$, $[OH^-] = 7.41\times 10^{-8}$)
3. What is the pH of a 1.0×10^{-4} M KOH solution? (Ans. pH = 10)
4. What is the pH of a solution if the $[H_3O^+]$ is 6.7×10^{-4}M. (Ans. pH = 3.17)
5. What is the pH of a solution for which $[OH^-]$ is 0.15M. (Ans. pH = 13.2)

Descriptive Questions

1. (a) What is Bronsted–Lowery acids and bases? Explain it with suitable examples.
   (b) Write equations and indicate the conjugate acid – base pairs for the following; (i) Acetic acid and water, (ii). Ammonia and hydrochloric acid
   (c) Justify that NH_3 is a base according to Lewis concept.
2. (a) Define buffer solution. What is buffer action and show with equations how a buffer system works?
   (b) What are the applications of buffers solutions?
   (c). Justify that buffer solution resists changes in pH, when a small amount of

an acid or a base is added.

3. (a) Briefly describe the leveling effect.
   (b) What is the relationship between K_a and K_b?
   (c) Write the equation relating K_a for a weak acid and K_b for its conjugate base. Use NH_3 and its conjugate acid NH_4^+ to derive the relationship between K_a and K_b.
4. (a) What is meant by the term amphoteric? Give an example of a substance or ion with amphoteric characteristics.
   (b) Define pH, pOH, pK_a and pK_b.
   (c) Explain ionization constant of water and calculate pH and pOH in aqueous medium using given K_w values.
5. (a) Define salt hydrolysis. Categorize salts according to how they affect the pH of a solution.
   (b) (i) What are conjugate acids and bases? Give the conjugate bases of the following acids; $HClO_4$, HCN, H_2CO_3, NH_4^+
   (ii) Classify as acids and bases giving reasons; BF_3, NH_3, NH_4^+, Ag^+, CaO, KCN, H_2S, SO_4^{2-}, Na^+, Cl^-
   (iii) Classify the following as Lewis acid or Lewis base; CO_2, H_2O, SO_2, I^-, NH_3, OH^-, BCl_3

PROJECT:

i. Arrange the following common substances in order of increasing pH:

Eggs	Apple	Tomato	Milk	Banana
Potatoes	Lemon	Shampoo	Water	Carbonated drink

ii. Group Work and Discussion
- Make a buffer solution in the laboratory.
- Record the pH of the buffer solution.
- Add small amount of strong acid to the buffer solution and record the pH of the solution.
- Add small amount of the strong base to the buffer solution and record the pH of the solution.
- Explain how such solution maintains a constant pH, even with the addition of small amounts of strong acid or strong base.
- Present your group work in the class and answer the questions of your classmates.